Measuring effective diffusivities in porous pellets: experimental procedures and FFT calculations

James Edward Klein
Iowa State University

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Experimental procedures and FFT calculations

by

James Edward Klein

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**NOMENCLATURE**

- **A**: cross-sectional area of pellet, \( \text{m}^2 \)
- **C**: concentration, moles/\( \text{m}^3 \)
- **C_a**: concentration in macropores, moles/\( \text{m}^3 \)
- **C_A**: concentration of species A, moles/\( \text{m}^3 \)
- **C_c**: concentration in column, moles/\( \text{m}^3 \)
- **C_e**: experimental gas concentration measured by TCD, moles/\( \text{m}^3 \)
- **C_i**: concentration in micropores, moles/\( \text{m}^3 \)
- **C_U**: concentration of tracer in \( V_U \), moles/\( \text{m}^3 \)
- **C_L**: concentration of tracer in \( V_L \), moles/\( \text{m}^3 \)
- **C_m**: concentration of tracer predicted by model, moles/\( \text{m}^3 \)
- **C_O**: concentration of tracer pulse, moles/\( \text{m}^3 \)
- **C_1**: concentration of tracer in media 1, moles/\( \text{m}^3 \)
- **C_2**: concentration of tracer in media 2, moles/\( \text{m}^3 \)
- **D_a**: effective diffusivity in macropores, \( \text{m}^2/\text{sec} \)
- **D_{AB}**: binary molecular diffusivity, \( \text{m}^2/\text{sec} \)
- **D_{BET}**: average BET surface area spherical particle diameter, \( \mu \text{m} \)
- **D_e**: effective diffusivity, \( \text{m}^2/\text{sec} \)
- **D_i**: effective diffusivity in micropores, \( \text{m}^2/\text{sec} \)
- **D_{KA}**: Knudsen diffusivity of gas A, \( \text{m}^2/\text{sec} \)
- **D_{ring}**: I.D. of pellet ring, O.D. of pellet, m
- **D_{SED}**: sedigraph equivalent spherical particle diameter, \( \mu \text{m} \)
- **D_{SED}**: average sedigraph equivalent spherical particle diameter, \( \mu \text{m} \)
- **D_{SEM}**: average SEM spherical particle diameter, \( \mu \text{m} \)
- **D_J(r)**: composite diffusivity in a capillary, \( \text{m}^2/\text{sec} \)
\( \bar{D}_{\text{TEM}} \) average TEM spherical particle diameter, \( \mu m \)
\( D_x \) axial dispersion coefficient in packed column, \( m^2/sec \)
\( D_1 \) effective diffusivity in media 1, \( m^2/sec \)
\( D_2 \) effective diffusivity in media 2, \( m^2/sec \)
\( F \) forcing function of tracer input, mole-sec/m^3
\( F_{\text{ave}} \) average flow rate = \( (F_1 + F_2) / 2 \), \( m^3/sec \)
\( F_U \) packed column inlet or upper chamber flow rate, \( m^3/sec \)
\( F_L \) lower chamber flow rate, \( m^3/sec \)
\( \text{FRACTM} \) fraction of \( (V_U - V_{\text{cone}}) \) that is well mixed in the CMDWKDC model
\( G \) moles of tracer in input pulse, moles
\( H_U \) \( D_e \tau_U / (L^2 \varepsilon_p) \)
\( H_L \) \( D_e \tau_L / (L^2 \varepsilon_p) \)
\( k_a \) reaction rate constant in macropores, \( \text{sec}^{-1} \)
\( k_{\text{ads}} \) adsorption rate constant, \( m^3/kg\text{-sec} \)
\( k_f \) fluid-to-solid mass transfer coefficient, \( m/sec \)
\( k_I \) reaction rate constant in micropores, \( \text{sec}^{-1} \)
\( K_{\text{ads}} \) adsorption equilibrium constant for the tracer, \( m^3/kg \)
\( K_D \) \( D_1 / D_2 \)
\( K_L \) \( \dot{A}D_e / (L F_L) \)
\( K_U \) \( \dot{A}D_e / (L F_U) \)
\( K_x \) \( L_1 / L_2 \)
\( K_\varepsilon \) \( \varepsilon_1 / \varepsilon_2 \)
\( L \) pellet length, m
\( L_{\text{cone}} \) cone depth into ring, m
\( L_{\text{ring}} \) length of pellet holding ring, m
LVU  
height of cone above pellet, m

LVUM  
fractional length of LVU for ideal mixing, m

LVUD  
fractional length of LVU for gas diffusion, m

L_1  
= (LVU)FRACTM for CMDWKDC model

L_2  
= L_1 + L for CMDWKDC model

LR  
pellet length-to-radius ratio

m_n  
n\textsuperscript{th} moment, sec\textsuperscript{n}

m_n(p)  
n\textsuperscript{th} weighted moment, sec\textsuperscript{n}

M  
strength of input pulse, \( = \frac{G}{F_U} = C_0t_{inj} \), mole-sec/m\textsuperscript{3}

M_A  
molecular weight of gas A

M_B  
molecular weight of gas B

M_1  
\( (L^2\varepsilon_2\lambda)^{1/2} \)

M_2  
\( A\varepsilon_2^{1/2} \)

M_6  
\( (D_1\varepsilon_1)^{1/2} \)

n_a  
concentration of adsorbing gas in the macropores, moles/kg

n_i  
concentration of adsorbing gas in the micropores, moles/kg

N  
number of discrete data points

N_a  
diffusional flux to macropores, moles/m\textsuperscript{2}-sec

N_A  
diffusional flux of A in capillaries, moles/m\textsuperscript{2}-sec

N_{Ae}  
effective diffusional flux of A, moles/m\textsuperscript{2}-sec

N_B  
diffusional flux of B in capillaries, moles/m\textsuperscript{2}-sec

N_i  
diffusional flux to micropores, moles/m\textsuperscript{2}-sec

P  
pressure, Pa

P_{Hg}  
mercury porosimetry pressure, Pa

P_s  
saturation pressure of adsorbing gas, Pa
\( P_1 = 1/(D_e)^{1/2}, \text{(sec/m}^2\text{)}^{1/2} \)

\( P_2 \) iterated lag-time parameter, sec

\( P_3 \) iterated square-wave pulse time, sec

\( r \) pore radius, nm

\( r_a \) radial coordinate in macropores, m

\( r_{cy} \) radius of cylindrical capillary, nm

\( r_j \) radial coordinate in micropores, m

\( r_{\text{max}} \) maximum pore radius for mercury intrusion, nm

\( r_{\text{mean}} \) volume-averaged mean pore radius, nm

\( r_{\text{min}} \) minimum pore radius for mercury intrusion, nm

\( r_{\text{mode}} \) modal radius for mercury porosimetry pore size distributions, nm

\( r_{xna} \) reaction rate in macropores, moles/m\(^3\)-sec

\( r_{xnj} \) reaction rate in micropores, moles/m\(^3\)-sec

\( R_a \) spherical radius of macroporous pellet, m

\( R_e \) Reynolds number = \( 2R_aU/\nu \)

\( R_g \) gas constant, 8.314 m\(^3\)-Pa/mol-K

\( R_i \) spherical radius of microporous particle, m

\( s \) Laplace transform variable, sec\(^{-1}\)

\( Sc \) Schmidt number = \( \nu/D_{AB} \)

\( SF \) scale factor, volt-m\(^3\)/mole

\( S_g \) gas adsorption surface area, m\(^2\)/kg

\( Sh \) Sherwood number = \( 2R_a k_f/D_{AB} \)

\( t \) time, sec

\( t_{\text{inj}} \) injection time, sec

\( t_{\text{lagd}} \) dead-volume lag-time, sec
\( t_{lagm} \) moment method lag-time; \( t_{lagd} + t_{inj}/2 \), sec
\( T_K \) temperature, Kelvin
\( U \) superficial velocity of gas in column, m/sec
\( V \) volume of mercury, \( m^3/\text{kg of sample} \)
\( V_{cone} \) volume tracer dispersion cone, \( m^3/\text{kg} \)
\( V_{DU} \) upper dead volumes, \( m^3 \)
\( V_{DL} \) lower dead volumes, \( m^3 \)
\( V_{GC} \) internal volume of GC valve, \( m^3 \)
\( V_{inj} \) volume of injected tracer, \( V_{GC} + V_{loop} \), \( m^3 \)
\( V_L \) lower cell volume, \( m^3 \)
\( V_{loop} \) volume of sample loop, \( m^3 \)
\( V_{max} \) volume of intruded mercury at 414 MPa, \( m^3/\text{kg of sample} \)
\( V_P \) pore volume, \( m^3/\text{kg of sample} \)
\( V_U \) upper cell volume, \( m^3 \)
\( x_{He} \) mole fraction of He in tracer
\( y_A \) mole fraction of gas A in capillary
\( y_e \) experimental data, volts
\( y_m \) model results, volts
\( Z \) \( = (s)^{1/2} \)

**Greek**
\( \alpha \) \( 1 - (M_A/M_B)^{1/2} = 1 + N_A/N_B \)
\( \alpha_i \) \( \rho_i L_1, \ i=1,2 \)
\( \beta_i \) \( \rho_i L_2, \ i=1,2 \)
\( \psi_i \) \( (s/\lambda_i)^{1/2}, \ i=1,2 \)
\( \gamma_{Hg} \) surface tension of mercury, dynes/m\(^2\)
\( \Gamma \) \( \frac{D_2 \psi_2}{D_1 \psi_1} \)

\( \Delta t \) time spacing between data points, sec

\( \Delta \mu_1 \) difference in \( \mu_1 \) values for two pellets of different length

\( \Delta \mu_{1\infty} \) \( \Delta \mu_1 \) as \( F_U, F_L \) go to infinity

\( e_a \) porosity in macropore region

\( e_c \) void fraction in packed column

\( e_i \) porosity in micropore region

\( e_p \) pellet porosity

\( e_{pg} \) pellet porosity determined geometrically

\( e_{pm} \) pellet porosity from mercury porosimetry experiments

\( e_1 \) porosity in media 1

\( e_2 \) porosity in media 2

\( \phi_1 \) \( \sinh(\psi_1 x) \)

\( \lambda_1 \) \( D_1 / e_1 \)

\( \lambda_2 \) \( D_2 / e_2 \)

\( \mu_n \) \( n^{th} \) absolute moment, sec\(^n\)

\( \mu_n^i \) \( n^{th} \) central moment about the mean, sec\(^n\)

\( \mu_n^{(p)} \) \( n^{th} \) absolute weighted moment, sec\(^n\)

\( \mu_n^{(p)} \) \( n^{th} \) central weighted moment about the mean, sec\(^n\)

\( \mu_{nLi} \) \( n^{th} \) absolute moment of \( C_L \) for an impulse function, sec\(^n\)

\( \mu_{nLS} \) \( n^{th} \) absolute moment of \( C_L \) for square-wave function, sec\(^n\)

\( \mu_{nLB} \) \( n^{th} \) absolute moment of \( C_L \) for bypass function, sec\(^n\)

\( \mu_{1LC} \) corrected experimental value of \( \mu_{1L} \), sec

\( \mu_{1LE} \) experimentally measured value of \( \mu_{1L} \), sec

\( \mu_{1\infty} \) value of \( \mu_1 \) as \( F_U, F_L \) go to infinity
\( \nu \) \hspace{1cm} \text{kinematic viscosity, m}^2/\text{sec}

\( \Pi_1 \) \hspace{1cm} AD_1/F_U, \text{m}

\( \Pi_2 \) \hspace{1cm} AD_2/F_L, \text{m}

\( \rho_a \) \hspace{1cm} \text{apparent density of pellet, kg/m}^3

\( \rho_i \) \hspace{1cm} \text{apparent density of microporous particle, kg/m}^3

\( \rho_{\text{pellet}} \) \hspace{1cm} \text{geometric density of a pellet, kg/m}^3

\( \rho_{\text{Hg}} \) \hspace{1cm} \text{density of mercury, kg/m}^3

\( \rho_{\text{ZnS}} \) \hspace{1cm} \text{density of ZnS, kg/m}^3

\( \tau \) \hspace{1cm} \text{tortuosity factor}

\( \tau_D \) \hspace{1cm} \text{characteristic diffusion time} = L^2 \varepsilon_p / D_e, \text{sec}

\( \tau_U \) \hspace{1cm} \text{upper chamber residence time} = V_U/F_U, \text{sec}

\( \tau_L \) \hspace{1cm} \text{lower chamber residence time} = V_L/F_L, \text{sec}

\( \theta_{\text{Hg}} \) \hspace{1cm} \text{mercury contact angle, degrees}

\( \theta_i(x) \) \hspace{1cm} \cosh(\psi_i x)
I. INTRODUCTION

"The prediction and correlation of fluxes for diffusion and flow of gases through porous solids, such as catalysts and adsorbents, are of considerable importance" (Youngquist, 1970). In adsorption processes as well as in catalytic and non-catalytic reactions, the rate of the overall process can be controlled, or limited, by the rate at which gases diffuse through the complex structure of a porous solid. The rate of mass transfer is characterized by an effective diffusion coefficient, $D_e$, or as it is commonly called, the effective diffusivity. $D_e$ is defined as the ratio of the flux of a diffusing species divided by the concentration gradient of that diffusing species. The qualifier "effective" indicates that the rate of transport induced by the concentration gradient is hindered by the non-void parts of the porous network.

For a gas-solid reaction of the type

$$A(s) + bB(g) = cC(s) + dD(g), \quad (1)$$

the overall reaction may proceed through the following individual steps (Gorring and deRosset, 1964):

1. Gas-phase mass transfer of the gaseous reactant from the bulk of the gas stream to the external surface of the solid.
2. Diffusion of the gaseous reactant through the pores of the solid.
3. Adsorption of the gaseous reactant on the solid surface.
4. Chemical reaction at the surface of the solid.
5. Desorption of the gaseous product from the surface.

6. Diffusion of the gaseous product through the pores of the solid.

7. Gas-phase mass transfer of the gaseous product from the external surface of the solid to the bulk of the gas stream.

The goal of the researcher studying gas-solid reactions is to understand and to be able to model these reactions so that prediction of conversion-time curves of the reacting solid can be obtained under a variety of reaction conditions. What are needed to reach this goal are: (1) accurate models of the reaction being investigated, (2) the corresponding rate constants associated with the proposed reaction, (3) diffusion data for modeling the flow of gases in and out of the solid, and (4) a knowledge of the structural properties of the solid under various reaction conditions.

In the production of zinc, the roasting of ZnS to ZnO is an important step in the process. The reaction in the roasting operation is

\[ \text{ZnS} + \frac{3}{2} \text{O}_2 = \text{ZnO} + \text{SO}_2 \]  

(2)

The zinc is obtained in a separate coking reaction of the ZnO. Although the kinetics of the roasting reaction are important, diffusional transport of the gases limit the overall reaction rate when temperatures exceed approximately 750 to 830°C (Frank, 1985).

Industrially, the reaction is carried out at higher temperatures and the understanding of the mass transfer rates through the porous structure becomes essential.
An apparatus that is commonly used to measure effective diffusivities is the dynamic Wicke-Kallenbach diffusion cell (DWKDC). In the experimental procedure, a cylindrical pellet is held between two chambers which have the same reference gas flowing through them. A pulse of diffusing gas is introduced into the stream entering the upper chamber and the gas that diffuses through the pellet is monitored by a detector connected to the exit stream leaving the lower chamber of the diffusion cell. De values are determined from analysis of this measured response.

The most commonly used method for analyzing response curves is the method of moments. By calculating the moments of the measured response curve and comparing these moments to the theoretical moments of a diffusion model for the cell, effective diffusivities can be calculated. The method of moments has some short-comings and an alternate procedure, parameter determination in the frequency, or Laplace transform, domain, has been used in this work. Here, the experimental data are transferred to the frequency domain via the fast-Fourier transform, FFT, and the sum-of-square error between the model and the experimental data is minimized by varying the parameters in the model: one of which is the effective diffusivity.

Although the DWKDC has been used to determine De values, the effect of different experimental conditions and procedures on the value of De calculated has not been investigated. Here, the effect of the experimental apparatus design, the shape of the sample pulse, the size of the sample loop, the concentration of the tracer gas, and the length
of the pellet on the value of $D_e$ calculated, has been investigated. Comparison of the $D_e$ values calculated by the FFT procedure and the method of moments will be compared and the superiority of the FFT procedure over the method of moments will be shown.
II. LITERATURE REVIEW

A. Basic Definitions

Before proceeding with a review of the literature, some of the terminology used will be defined. The effective diffusivity, \( D_e \), is a parameter used to relate the flux of a diffusing species to the concentration gradient of the diffusing species when diffusion occurs in porous media. A mass balance on a rectangular, differential element in a porous pellet will yield

\[
\frac{\partial}{\partial t} (C \varepsilon_p \Delta x \Delta y \Delta z) = -D_e \frac{\partial C}{\partial x} \Delta y \Delta z + D_e \frac{\partial C}{\partial x} \Delta y \Delta z + \text{(other terms)}
\]

(3)

where \( C \) = concentration in the pore space, and \( \varepsilon_p \) = porosity of the pellet.

As shown in this equation, the diffusional flux is based on the entire cross-sectional area of the differential element.

When discussing the use of dynamic methods to determine diffusivity values, a description of the forcing function, \( F(t) \), used to perturb a system from its steady-state condition, must be described. For an impulse function, a square wave pulse, and a step function, \( F(t) \) takes the following forms:

\[
F(t) = M \delta(t) \quad \text{for an impulse function,}
\]

(4)

\[
F(t) = \frac{M}{t_{\text{inj}}} \quad 0 < t < t_{\text{inj}}
\]

(5)

For a square wave pulse, and

\[
F(t) = C_0 \quad t > 0
\]

(6)

for a step function,
where $\text{M} = \text{strength of the input pulse}$,

\[ t_{\text{inj}} = \text{tracer injection time, and} \]

\[ C_0 = \text{concentration of the tracer pulse}. \]

For a bypass experiment or bypass run, where the injected sample bypasses a packed column or diffusion cell, the discrete, collected data were used to represent $F(t)$. For an impulse function, a square wave pulse, and a bypass function, conservation of mass dictates

\[ G = \int_0^\infty F(t)dt = C_0V_{\text{inj}}. \quad (7) \]

When a system is perturbed from steady-state conditions, the change in concentration detected and recorded will be called the response curve for the experiment. For a step-change forcing function, the response curve is usually referred to as the breakthrough curve (BTC). For a finite size pulse injected into a system, the response curve is called the chromatographic response curve (CRC). The relationship between the BTC and CRC resulting from an impulse forcing function is given by (Levenspiel, 1972)

\[ \frac{dC_{\text{BTC}}}{dt} = C_I. \quad (8) \]

To obtain the response curve for some arbitrary forcing function, the response from an impulse forcing function is convoluted with the forcing function:

\[ C(t) = \int_0^\infty \frac{tF(t-t')C_I(t')dt'}{M} \quad (9) \]

For a CRC, moments are a set of descriptive constants which are
useful for measuring its properties. For a concentration distribution function \( C(t) \), the \( n^{th} \) moment of the distribution is given by

\[
m_n = \int_0^\infty C(t)t^n dt
\]

From experimental data, moments can be calculated quite easily using various quadrature routines. If the Laplace transform (LT) of \( C(t) \) is available, the \( n^{th} \) moment is related to the LT solution by

\[
m_n = (-1)^n \lim_{s \to 0} \frac{d^n \overline{C}}{ds^n}
\]

where \( \overline{C} \) is the LT of \( C(t) \).

B. Methods for Measuring Effective Diffusivities

Experimental methods for determining \( D_e \) values can be divided into steady-state, dynamic, and chemical reaction procedures. For steady-state measurements, the main experimental procedure has been the Wicke-Kallenbach diffusion cell (WKDC). The types of transient procedures are more numerous and the procedure used in this work is a dynamic version of the WKDC: it is called the dynamic Wicke-Kallenbach diffusion cell (DWKDC). Diffusivities determined during chemical reactions will be discussed later in this section. Even though the experiments performed in this work were done using a single-pellet technique, some of the work that has used and analyzed CRC obtained from packed, or chromatographic, columns will be reviewed. This is done since the packed column experiments preceded the dynamic, single pellet technique; many of the same ideas that were applied to the analysis of CRC of packed columns carry over to the analysis of single
pellet response curves. Furthermore, by discussing packed column experiments, the advantages of a single pellet technique will become clear.

1. Wicke-Kallenbach diffusion cell

What is referred to as a Wicke-Kallenbach diffusion cell was first developed by Wicke and Kallenbach (1941) and was later modified to handle pellets of different geometries by Weisz (1957). A schematic drawing for the diffusion of gases A and B in a pellet are shown in Figure 1. At steady-state conditions, and at constant pressure, the effective flux through the pellet can be written as

\[ N_{Ae} = - \frac{P}{R_g T_K} D_e \frac{dy_A}{dx} \]  

where \( N_{Ae} \) = effective flux of gas A,

\( P \) = pressure,

\( R_g \) = gas constant,

\( T_K \) = temperature, and

\( y_A \) = mole fraction of A.

Usually \( D_e \) is assumed to be composition independent and is calculated from experimental data using

\[ N_{Ae} = - \frac{P}{R_g T_K} D_e \frac{(y_{AL} - y_{AO})}{L} \]  

where \( y_{AO} \) = mole fraction of A at \( x = 0 \),

\( y_{AL} \) = mole fraction of A at \( x = L \), and

\( L \) = length of the pellet.

Knowing the gas stream compositions, gas stream flow rates, and the
Figure 1. Flow diagrams of steady-state and dynamic Wick-Kallenbach diffusion cells
cross-sectional area of the pellet, $N_{Ae}$ can be calculated and $D_e$ determined. Reviews of some of the works done using the WKDC are presented in Dogu (1986, pp. 440-441), Satterfield (1981, pp. 56-77), and Szekely et al. (1976, pp. 228-231). The main arguments against using $D_e$ values determined from steady-state measurements is that the steady-state $D_e$ values do not show the effect of dead-end pores; diffusivities determined using dynamic procedures are thought to include the effect of these dead-end pores (McGreavy and Siddiqui, 1980).

2. Packed beds

The most general case of mass transport of a gas or a liquid flowing through a fixed bed of particles is when a bimodal pore structure is present. This occurs, for example, when molecular sieve pellets consist of zeolite crystals imbedded in a clay matrix. The mass transfer of a tracer through the column can undergo dispersion in the inter-particle voids, bulk-flow-to-pellet transfer, intra-pellet diffusion into the macropores of the pellet, and intra-pellet diffusion in the pores of the zeolite particles. The tracer can also undergo adsorption and/or chemical reaction. The resulting differential equations for the general case are

for the column,

$$
\frac{\partial C_c}{\partial t} = D_x \frac{\partial^2 C_c}{\partial z^2} - \frac{\partial C_c}{\partial z} - 3 \frac{(1-\varepsilon_c)}{R_a} N_a^2,
$$

(14)
for the macropores,

\[
\frac{\partial C_a}{\partial t} = \frac{D_a}{\varepsilon_a} \left( \frac{\partial^2 C_a}{\partial r_a^2} + \frac{2}{r_a} \frac{\partial C_a}{\partial r_a} \right) - \frac{3(1-\varepsilon_a)}{\varepsilon_a} N_a - \rho_a \left( \frac{\partial n_a}{\partial t} + \frac{r_{xn_a}}{\rho_a} \right),
\]

(15)

and for the micropores,

\[
\frac{\partial C_i}{\partial t} = \frac{D_i}{\varepsilon_i} \left( \frac{\partial^2 C_i}{\partial r_i^2} + \frac{2}{r_i} \frac{\partial C_i}{\partial r_i} \right) - \rho_i \left( \frac{\partial n_i}{\partial t} + \frac{r_{xn_i}}{\rho_i} \right),
\]

(16)

where \( C_c \) = concentration in column,
\( C_a \) = concentration in macropore region,
\( C_i \) = concentration in micropore region,
\( D_a \) = axial dispersion coefficient,
\( D_x \) = effective diffusivity in macropores,
\( D_i \) = effective diffusivity in micropores,
\( U \) = superficial velocity of gas in column,
\( \varepsilon_c \) = void-fraction in packed column,
\( \varepsilon_a \) = porosity in macropore region,
\( \varepsilon_i \) = porosity in micropore region,
\( r_a \) = radial coordinate in macroporous particle,
\( r_i \) = radial coordinate in microporous particle,
\( R_a \) = spherical radius of macroporous particle,
\( R_i \) = spherical radius of microporous crystal,
\( N_a \) = flux to macropores,
\( N_i \) = flux to micropores,
\( \rho_a \) = apparent pellet density,
\( \rho_i \) = apparent crystal density,
\( n_a \) = moles of tracer adsorbed on the solid in macropores,
nᵢ = moles of tracer adsorbed on the solid in micropores,
\[ \text{rxn}_a = \text{reaction rate in macropores, and} \]
\[ \text{rxn}_i = \text{reaction rate in micropores.} \]

The previous equations were derived assuming isothermal
conditions, negligible pressure drop along the length of the column,
and that the plug-flow dispersion model adequately represents the
deviation from plug-flow conditions. The possibility of an adsorbed
molecular species undergoing surface diffusion was also neglected.
Schneider and Smith (1968) show how surface diffusion can be
incorporated into the model and Tamon et al. (1985), and Riekert (1985)
discuss the surface diffusion phenomena.

Many times, the term \( D_e \) is referred to as the effective
diffusivity and the macropore and micropore qualifiers are used to
differentiate between diffusivity values for the different pore
structures. The symbol \( D_e \) will be used when discussing effective
diffusivity in general, and the subscripts \( a \) and \( i \) will be used when it
is necessary to distinguish between diffusivity values in the different
pore structures. For the ZnS system used in this study, the symbols \( D_a \)
and \( D_e \) can be used interchangeably.

The expressions used for \( N_a \) and \( N_i \) to couple together the previous
equations are

\[
N_a = D_a \left. \frac{\partial C_a}{\partial r_a} \right|_{r_a=R_a} = k_f (C_c - C_a) \left|_{r_a=R_a} \right., \quad \text{and} \]

(17)
where $k_f$ is the external mass transfer coefficient. For adsorption that is assumed to be a linear function of the adsorbed concentration, occurring at a finite rate, the reaction and adsorption terms are represented as

$$N_i = D_i \frac{\partial C_i}{\partial r_i} \bigg|_{r_i=R_i},$$

(18)

where $D_i$ is the diffusion coefficient, $C_i$ is the concentration, and $R_i$ is the boundary radius.

The boundary conditions used in conjunction with the previous equations are

$$\frac{\partial C_a}{\partial r_a} \bigg|_{r=a} = 0$$

(21)

$$\frac{\partial C_i}{\partial r_i} \bigg|_{r_i=0} = 0$$

(22)

where $C_a$ is the concentration in the macropore region, $C_i$ is the concentration in the micropore region, and $n_a$ and $n_i$ are the adsorbed concentrations in the macropore and micropore regions, respectively.
The expression in Equation (22) assumes that $D_a >> D_i$. The initial conditions used are of zero concentration throughout the system at time zero, and that some type of forcing function is introduced at the entrance of the column to perturb it from its steady-state conditions.

In general, no closed-form solution for the previously described set of equations is available; however, analytical solutions for certain simplified models are available (Rasmuson and Neretnieks, 1980, Rasmuson, 1981, Huang et al., 1984, and Schneider, 1984). The LT procedure is usually used to solve the set of equations and the moments of the concentration in the column are calculated using Equation (11). The moments generated from the LT solution contain the parameters $D_x$, $D_a$, $K_{ads}$, $k_f$, $K_{ads}$, $k_a$, and $D_i$. The procedures used to calculate these parameters from the moment expressions for special cases of Equation (14) through Equation (23), will be briefly discussed.

The simplest case of the general problem is trying to determine the dispersion characteristics of flow through a bed of non-porous particles. In this case, $N_a$ is zero and only Equation (14) is solved. For certain choices of boundary conditions at the beginning and end of the column, an analytical solution to Equation (14) is possible. When no analytical solution is possible, van der Laan (1957) and Hsu and Dranoff (1986) discuss the effects that different boundary conditions have on the solution to the problem.

The problem of trying to account for the effects of dispersion has

\[ C_1 \bigg|_{x=x_a} = C_a \]  

(23)
been investigated for years. Hsiang and Haynes (1977) state that
treatment of axial dispersion effects has been in the chemical
engineering literature for over three decades. The large number of
articles appearing in the literature in recent years indicates that the
phenomena is still not well understood. Consistent column repacking
has been a problem for Hashimoto and Smith (1973, 1974) as well as the
problem of the channeling of flow through the beds (Suzuki and Smith,
1972b). The effects of channeling has been investigated by Oliveros
and Smith (1982), but this idealized study does not solve the
channeling problem. The effect of particle size and bed length on
axial dispersion has been investigated by Han et al. (1985), but
correlations developed still appear to apply only for the particular
system being investigated at the time.

For the case where micropores are absent from the pellets, $N_i$ in
Equation (15) is zero. Suzuki and Smith (1971) generate the LT
solution to this problem which includes adsorption and reaction in the
macropores and the first two moments obtained from the LT solution.
The authors review previous works performed on packed beds where
different mass transfer resistances, adsorption, and reaction terms,
were deleted or neglected.

The moments calculated by Suzuki and Smith (1971) contain six
parameters: $D_x$, $k_f$, $D_a$, $k_{ads}$, $k_a$, and $k_{ads}$. The experimental
procedure used to generate data for evaluating these parameters is to
obtain experimental moments at different fluid velocities through the
column for different size particles. The authors admit that the moment
expressions are too complicated to use effectively with experimental data and to make the problem more tractable, one or two of the three transport processes represented by $D_X$, $k_f$, or $D_a$, need to be neglected. The authors discuss special cases of their general problem and the methods of using CRC and moments to evaluate the relative importance of adsorption and reaction.

The first papers to develop expressions for packed columns possessing pellets with a bimodal pore structure were by Hashimoto and Smith (1973), Ma and Mancel (1973), and Haynes and Sarma (1973). In Equation (15), adsorption and reaction in the macropores is deleted and reaction in the micropores is not considered. In the model developed by Haynes and Sarma (1973), adsorption is assumed to be instantaneous and reversible and Equation (16) and Equation (20) for their model would be in slightly different forms.

This model, with the adsorption process given by Equation (20), without chemical reaction, contains the parameters $D_X$, $k_f$, $D_a$, $k_{ads}$, $K_{ads}$, and $D_i$. As done before, experimental moments are calculated using different gas velocities through the column for different size pellets. Hashimoto and Smith (1973, 1974) and Ma and Mancel (1973) describe the procedure used to obtain the six parameters from experimental moments. Haynes (1975) discusses experimental procedures that can be used to increase the reliability of the parameter values obtained when analyzing CRC of packed columns.

One of the problems in using moments to calculate model parameters is that a slight drift in the baseline of a CRC will cause significant
errors in the calculated moments. The calculation of first moments is fairly reliable, but first moments for packed beds only contain the parameter $K_{ads}$. Second moments are sensitive to small drifts in the baseline and are less reliable than first moments (Suzuki and Smith, 1972b, and Sarma and Haynes, 1974). Calculation of moments higher than order two are considered unreliable, but third moments have been used (Gelbin et al., 1982).

Even if the moments of the CRC could be calculated accurately, errors in calculating or estimating $k_f$ and $D_x$ have a significant affect on the value of $D_a$ calculated. $k_f$ is usually estimated from a correlation such as

$$Sh = \frac{2R k_f}{D_A} = 2.0 + 0.60Re^{1/2}Sc^{-1/3},$$

(24)

where $Sh$ = Sherwood number,

$Re$ = Reynolds number, and

$Sc$ = Schmidt number.

Hashimoto and Smith (1973, 1974) have used the value of 1.45 instead of 0.60 in Equation (24). For low flows, the approximation of $Sh = 2.0$ is often used. Sarma and Haynes (1974) had significant resistances to mass transfer and Hashimoto and Smith (1974) estimate errors in $k_f$ give an uncertainty in $D_a$ of roughly 25%.

$D_x$ is usually calculated from one of two procedures. The first is to pack a column with non-porous particles and develop a correlation between $D_x$ and fluid velocity. The values of $D_x$ obtained with this procedure are then used in the calculations of the other parameters.
The second procedure is to plot a modified form of the second moment expression versus the reciprocal of the fluid velocity squared. From this plot, $D_x$ can be determined from the slope of the line. Even if reliable values for $D_x$ are obtained, the effects of axial dispersion can significantly affect the value of $D_a$ calculated. Hashimoto and Smith (1973) state that errors in evaluating the effects of axial dispersion had the largest influence on calculating $D_a$. Sarma and Haynes (1974) had the correction for axial dispersion from between 35 to 75% of the total variance of the CRC for the system used in their study and this reduces the precision of their $D_a$ calculations.

Suzuki and Smith (1972b) discovered that channeling in the bed, caused by the shifting of the bed, can cause a large increase in axial dispersion. $D_x$ was also found to be dependent on velocity and on particle size. Hashimoto and Smith (1973) state that $D_x$ is very sensitive to the packing of the column and it can deviate significantly from one study to the next. Although analysis of experiments performed on packed columns give reasonable agreement between $K_{ads}$ values obtained using this and other methods, the calculation of the other parameters in the model are complicated by the necessity of calculating second moments and the inclusion of $D_x$ and $k_f$ in the model. The dynamic version of the WKDC, described next, eliminates $D_x$ and $k_f$ from the moment expressions and $D_a$ appears in the expression for first moment. For these reasons, the dynamic diffusion cell is a favorable procedure to use when calculating $D_a$ values.
3. Dynamic Wicke-Kallenbach diffusion cell

Although most of the credit for the development of what is referred to as the dynamic Wicke-Kallenbach diffusion cell (DWKDC) is given to Dogu and Smith (1975), similar experimental designs had been used earlier by other workers (Gibilaro et al., 1970, and Wakao, 1974). A flow diagram of a DWKDC is also shown in Figure 1. Instead of having two different gas compositions flow over the faces of the pellet, as was done for the steady-state WKDC, the same reference gas is passed over the exposed faces of the pellet. A pulse of the diffusing, or tracer, gas is introduced into the stream flowing into the upper chamber of the cell; the gas that diffuses through the pellet is detected by monitoring the stream of gas that leaves the bottom of the diffusion cell. Suzuki and Smith (1972a) had used a diffusion cell where the detecting element was placed in the lower chamber of the diffusion cell, in the absence of gas flow, but the signal obtained was noisy and unstable. An advantage the dynamic experiments have over the steady-state experiments is that the dynamic experiments can be run faster than the steady-state experiments. It is also argued that dynamic experiments will reflect the effects of dead-end pores that steady-state experiments miss.

As was done for a column packed with particles, the most general differential equations will be written and simplifications of these equations will be discussed. The differential equations are
for the upper chamber,
\[ \frac{\partial C_U}{\partial t} = F_U \frac{\partial C_U}{\partial t} - F_U C_U + AD_a \frac{\partial C_U}{\partial x} \mid_{x=0}, \] (25)

for the pellet,
\[ \frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} - 3 \left( \frac{1-\varepsilon}{R} \right) N_i - \rho_a \left( \frac{\partial n_a}{\partial t} + \frac{\partial n_a}{\partial x} \right), \] (26)

for the micropores,
\[ \frac{\partial C_i}{\partial t} = D_i \left( \frac{\partial^2 C_i}{\partial r_i^2} + 2 \frac{\partial C_i}{\partial r_i} \right) - \rho_i \left( \frac{\partial n_i}{\partial t} + \frac{\partial n_i}{\partial r_i} \right), \] and (27)

for the lower chamber,
\[ \frac{\partial C_L}{\partial t} = -F_L C_L - AD_a \frac{\partial C_L}{\partial x} \mid_{x=L}. \] (28)

where \( C_U \) = concentration of tracer in upper chamber,
\( C_L \) = concentration of tracer in lower chamber,
\( V_U \) = volume of upper chamber,
\( V_L \) = volume of lower chamber,
\( A \) = cross-sectional area of the pellet,
\( L \) = length of the pellet,
\( F_U \) = flow rate into upper chamber, and
\( F_L \) = flow rate into lower chamber.

When comparing these equations to those derived for a packed column, the two mass conservation equations for the upper and lower chamber replace the equation for mass conservation in a section of the column. This elimination of \( D_x \) from the conservation equations makes the DWKDC
an attractive procedure for measuring effective diffusivities.

Equation (26) is similar to Equation (15) only Equation (15) is written for a spherical particle; Equation (27) for the micropores is the same as Equation (16).

The corresponding boundary conditions for the DWKDC model are

\[ -D_a \frac{\partial C_a}{\partial x} \bigg|_{x=0} = k_f (C_U - C_a) \bigg|_{x=0}, \quad (29) \]

\[ -D_a \frac{\partial C_a}{\partial x} \bigg|_{x=L} = k_f (C_a) \bigg|_{x=L} - C_L, \quad (30) \]

\[ \frac{\partial C_i}{\partial r_i} \bigg|_{r_i=0} = 0, \quad \text{and} \]

\[ C_i \bigg|_{r_i=R_i} = C_a. \quad (32) \]

It has been assumed in deriving these equations that mixing is vigorous in the upper and lower chambers. In most model derivations, mass transfer resistance between the gas and the pellet faces are assumed to be negligible and Equation (29) and Equation (30) reduce to

\[ C_U = C_a \bigg|_{x=0} \quad (33) \]

\[ C_L = C_a \bigg|_{x=L} \quad (34) \]

Initially, the gas concentrations are assumed to be zero throughout the system.

In most works, an impulse function has been used for the forcing function. In the earlier papers dealing with the DWKDC, the concentration of the tracer was assumed to be zero once the pulse had been introduced over the top of the pellet (Gibilisco et al., 1970, Wakao, 1974, Dogu and Smith, 1975, 1976, Hashimoto et al., 1976, and
Moffat, 1978). Not until the work of Burghardt and Smith (1979) was accumulation of tracer in the upper chamber included in the model. Once the complete mass balance in the upper chamber was included in the diffusion model, the complete moment expressions could be derived and the errors associated with neglecting terms in the model could be analyzed (Burghardt and Smith, 1979).

When the effective diffusivity in the macropores is the only parameter to be determined, the DWKDC has a distinct advantage over packed columns since $D_a$ appears in the expression for the first moment instead of in the expression for the second moment. For a non-adsorbing, non-reacting system, $D_a$ is the only unknown parameter in the expression for the first moment. However, when adsorption processes include the parameter $K_{ads}$, this parameter also appears in the expressions for the first moment.

For various combinations of adsorption and reaction in a pellet containing a unimodal pore structure, Dogu and Smith (1976) present first and second moment expressions which contain the reaction rate and adsorption parameters. Reaction rates and adsorption parameters have been determined using moment analysis of CRC obtained from a DWKDC (Ozan and Dogu, 1981, and Dogu et al., 1986). For a system with bidispersed pores, with no reaction or adsorption, $D_i$ appears in the expression for second moments (Hashimoto et al., 1976) and $D_i$ values have been determined using a DWKDC by Dogu and Ercan (1983) and Dogu et al. (1987).

Although the method of moments appears ideal for determining rate
parameters when analyzing results obtained from the DWKDC, there are problems. Since first moments are used for determining rate parameters, these values must be determined fairly accurately. One problem is to properly account for the dead-time corrections for the flow of gases to and from the diffusion cell. For short diffusion times, these corrections can be a significant part of the measured first moment and thus decrease the precision of the calculated diffusivity value (Ramachandran and Smith, 1978). As was stated before, the moment method is sensitive to noise and drift of the detector and this can still be a problem for first moments when experiments are performed which push the detection limits of the system.

4. **Diffusion-limited gas-solid reactions**

Since the reaction rate of the ZnS roasting reaction, at elevated temperatures, is limited by the diffusion of gases through the ZnO product layer, there are reaction models that will allow one to make estimates of $D_e$ values for the product layer. If the model used approximates the actual experimental conditions, conversion-time data can be used to estimate the $D_e$ values. Since the product layer is ZnO instead of ZnS, diffusivities obtained by this procedure can not be compared to the values obtained in this study. If a ZnO sample had been mounted for analysis in a DWKDC, the $D_e$ values obtained could be compared to those obtained from reaction model analysis.

Levenspiel (1972, pp. 364-366) presents the idealized case for an unreacted core model for spherical particles of unchanging size for
which diffusion through the ash layer controls the overall rate of reaction. Since the specific volumes of ZnS and ZnO are similar, this model may be an appropriate approximation of the physical process. Assuming that the shrinkage of the unreacted core of ZnS is much slower than the flow rate of O\textsubscript{2} to the unreacted core, and that the rate of O\textsubscript{2} transfer to the core can be described by an effective diffusivity, the time since the beginning of the reaction can be related to conversion by

\[ t_{\text{rxn}} = \frac{\rho_p R a}{6(2/3)D_{\text{e}O_2}} \left[ 1 - 3(1 - X_{\text{ZnS}})^{2/3} + 2(1 - X_{\text{ZnS}}) \right], \]  

(35)

where \( t_{\text{rxn}} \) = time since the beginning of the reaction, 
\( \rho_p \) = apparent density of the ZnO product layer, 
\( X_{\text{ZnS}} \) = conversion of ZnS, and 
\( C_{\text{O}_2} \) = concentration of O\textsubscript{2} outside the pellet.

The fraction 2/3 is from the stoichiometry of Equation (2). By monitoring the weight change of the reacting particle or the SO\textsubscript{2} production, with time, conversion-time data can be obtained and an effective diffusivity calculated.

Although the model is simple, Gorkarn and Doraiswamy (1971) found experimental time-conversion data fit well to the previously described model when mass transfer resistance through a stagnant layer of gas was incorporated into the model. In a subsequent paper, Gorkarn and Doraiswamy (1972) state that the \( D_e \) values obtained by taking a piece of the product layer and analyzing it in a WKDC were different than the values obtained when the product layer was crushed and pressed into
pellets that were analyzed in the WKDC: even when the total porosity of the pellets was the same. This showed that different $D_e$ values could be obtained for the same system when pellets were prepared using different procedures.

5. **Other methods**

Some other methods for determining $D_e$ values are, as coined by Biswas *et al.* (1986), the batch reservoir, the flow through reservoir, and the infinite reservoir techniques. Although these are alternate techniques for determining $D_e$ values, they are not used as frequently as the previously mentioned procedures and so will be discussed only briefly.

In the batch reservoir method, porous pellets are introduced into a well-stirred, constant volume apparatus. A known amount of sorbate gas is injected into the apparatus and the gas concentration in the vessel monitored periodically throughout the course of the experiment. By knowing the pellet size, the geometry of the vessel and the time history of the gas in the apparatus, the effective diffusivities for the system can be calculated (Ma and Lee, 1976).

The flow through reservoir technique was developed by Frost (1981). The author suspended zeolite particles in a well-mixed, known-volume chamber. The zeolite particles were equilibrated with a gas stream of known composition before a step change in the inlet gas concentration was made. By monitoring the gas composition flowing from the reservoir and by knowing the composition of the inlet gas stream, the uptake of gas by the zeolite particles could be inferred and the
diffusivity of the gas into the particles could then be calculated.

The infinite reservoir technique is more commonly known as a sorption-balance technique. A sample of a powder or a pellet is placed in a micro-, or quartz-spring, balance and the sample either held under vacuum or equilibrated with a gas of known composition. After equilibration, the sample is exposed to a step change in gas concentration and the sample's weight change is monitored as a function of time. By comparing the experimental sorption curve to the theoretical sorption curve, a diffusivity can be calculated. Ruthven and Loughlin (1971) discuss the problems in calculating $D_e$ values in molecular sieves when using an equivalent spherical diameter, instead of including the shape and size distribution of the crystals into the calculations.

C. Analysis Methods for Calculating Effective Diffusivities

Two similar papers, by Ramachandran and Smith (1978) and Smith (1984), discuss the different procedures for analyzing transient responses of different contacting devices. The analysis procedures are grouped into four classifications: 1) moment methods, 2) curve fitting in the time domain, 3) fitting in the frequency domain, and 4) fitting, or transfer function fitting, in the LT domain. Curve fitting in the time domain can be applied to non-linear processes, but the other procedures are limited to linear processes. The articles discuss the merits and disadvantages of the four analysis procedures. Wakao and Kaguei (1982, pp. 1-71) discuss the use of these different procedures and are strong supporters of determinations performed in the time
domain. Before the analysis procedures are presented, modifications of the experimental data must be discussed since the data are modified by performing data analysis.

When experimental data for a dynamic response curve are obtained, a certain amount of noise is present and drift in the baseline of the data can severely affect the value of parameters inferred from analysis of the response curve. Before analysis of this response curve is performed, the raw data are modified to account for the fact that a non-constant value of the baseline was obtained. For the types of forcing function inputs described previously, the models of these dynamic processes approach steady-state conditions as time goes to infinity, but experimental data collection is performed over a finite time interval. This truncation of the experimental data set can also affect the parameters determined from data analysis. Some of the procedures used in the literature for raw data modification will be discussed below and the raw data modifications done in this work are described in the Theory section.

MacDonald and Habgood (1972) discuss the modification procedure of the response curves they obtained from a packed column of zeolite particles. The baseline value used for the CRC was twice the half-width of the noise band above and below the average baseline value. Moments were calculated using baseline values that were above the previously described baseline by using a new base line that was 0.5% of the value of the maximum peak height. Consistent second moments were obtained using this procedure since the baseline was established above
the noise in the tail of the CRC. Schneider (1987) used a similar procedure and band widths of 0.25, 0.5, 1.0, and 2.0% of the peak maximum value were used. Second moments calculated this way were always less than the theoretical values obtained in the analysis of the problem.

Sater and Levenspiel (1966) modify the tail of their response curve to eliminate the problems associated with signal noise. It was assumed the the response of their data should decay exponentially and this assumption was used to modify and extend their experimental data. By plotting the experimental data to the right of the maximum of the CRC versus time on semi-logarithmic paper, a straight line was drawn through the data, extrapolated beyond the end of the data, and the equation for this line was used to generate the data for the tail section of their CRC. This data modification procedure gave negative values for positive parameters when used by Gomezplata and Brown (1968).

Curl and McMillian (1966) used a procedure similar to that of Sater and Levenspiel when they modeled their CRC by breaking it up into two parts: the first part being an impulse function and the second part being an exponential decay. Skopp (1984) presents a procedure for determining the optimum truncation time: the time after which the experimental data are truncated. The author suggests using a time domain model, which is a function of the moments, to generate the data values for the trailing data values of the response curve. Gomezplata and Brown (1968) plotted the natural logarithm of time versus chart
deflections of their recorder and used this straight line to fit the data: even though this plot had no theoretical foundation. Data modifications procedures such as these are to be avoided since the experimental data are made to match the model for the system instead of developing a model for the system which can explain the experimental data. Schneider (1987), Hsiang and Haynes (1977), and MacDonald and Habgood (1972) looked at modeling a CRC as a Gaussian distribution. The modeling of a CRC as a Gaussian curve was not very successful since the CRC only approaches a Gaussian shape in the limit as diffusion and dispersion go to zero (Haynes, 1975).

1. Moment methods

The greatest advantage of using experimental moments for determining rate parameters is that experimental moments are computationally very easy to calculate. After the CRC is obtained, experimental moments are calculated using Equation (10). Theoretical moments, calculated using Equation (12), show the various contributions made by the rate parameters to the overall moment expression. The disadvantage of the moment procedure is that the tail of the response curve, the region with the least accurate data, is weighted the heaviest in the experimental moment calculation. The method of using weighted moments, where a decreasing exponential weighting factor is included in the calculation of the experimental moment, was first used by Mixon et al. (1967) and the definition of the weighted moment is shown in Equation (40). This procedure reduces the heavy weighting of the tail of the experimental data, but the new problem of picking the
optimum value of the term in the exponential weighting factor, \( p \), is generated. Examples of empirical methods for picking values of \( p \) are shown by Anderssen and White (1971).

Once experimental moments are calculated, several procedures are available for determining \( D_e \) when using a DWKDC. The first procedure is to equate the first moment expression to the corrected experimental moment: the value of the experimental moment adjusted for the lag-times for gas flows to and from the diffusion cell and adjusted for the sample injection time as shown in Equation (101). In the absence of adsorption and reaction, \( D_e \) is the only parameter in the equating of the moments and its value can be calculated. Dogu and Smith (1975, 1976) and Wang and Smith (1983) used this procedure for several moments obtained at different flow rates and varied \( D_e \) to minimize the sum-of-squares error between the theoretical and corrected first moment expressions.

Another procedure that is similar to calculating \( D_e \) values by equating theoretical and corrected experimental moments is to repeat the previously described procedure for the limiting case of \( F_U \) and \( F_L \) going to infinity. The first theoretical moment for this case is designated as \( \mu_{1\infty} \) and is given by, in the absence of adsorption and reaction,

\[
\mu_{1\infty} = \frac{L^2 D_e}{6D_e}. \tag{36}
\]

The procedure used for obtaining an estimate of the limiting experimental moment is to plot the experimental, or corrected
experimental moment versus $F_L$, at constant $F_U$, and estimate an experimental value of $\mu_1$ from the extrapolation of the plot to infinite lower flow rate. The extrapolation of this plot gives uncertainty to the limiting value obtained and does not take into account flow rate dependence of the properties in the upper chamber.

A third way to use experimental moments is to calculate the difference in first moments for two pellets of different lengths run at the same experimental conditions. It is assumed in this method that the difference in the moments is caused by the interaction of the tracer in the length of a pellet equal to the difference in lengths between the two pellets. First moments calculated using this procedure are denoted as $\Delta \mu_1$. Dogu et al. (1986) and Dogu et al. (1987) have combined this and the previous procedure for calculating $D_e$. The $\mu_{1w}$ moments are obtained for two different length pellets and are subtracted from one another and are denoted $\Delta \mu_{1w}$.

The problem with using the method of moments, as mentioned before, is that the calculation of the moment value is affected by errors in data in the tail of the response curve. Just as experimental second moments are less reliable than first moments, first moments become less reliable than zeroth moments when noise and drift of the response curve increases; this problem is encountered when low concentrations of the tracer are being detected in experiments where long pellets are being used or low concentrations of the tracer gas are used in the injected samples. The calculations of moments by equating theoretical and corrected experimental moments suffers from the disadvantage of having
to make accurate estimates of the lag-time corrections for the experimental moments. For short pellets, this correction can be a significant portion of the measured moment. Difference-in-moment procedures appear to remove this problem, but the extrapolation of moments to infinite flows is still questionable.

2. Curve fitting in the time domain

In this procedure, parameters are determined by the matching of experimental response curves with theoretical concentration-time curves. If an analytical solution to the problem is available, parameters can be varied in the model until the error between the model and the data is minimized. If an analytical solution is not available, numerical integration of the conservation equations is necessary to obtain a time-domain estimate of the model. For multiple or complex conservation equations, significant computational effort may be required, as in the case of diffusion and adsorption in packed columns (Tan, 1986). The advantages of time domain fitting is that theoretical and experimental data can be compared for any point on the response curve: use of the entire response curve is not necessary. This procedure is superior to the moment method since the trailing data values can be eliminated from the data analysis procedure. Analytical solutions for the DWKDC are available (Dudukovic, 1982, and Do and Smith, 1984), and time domain fitting procedures for obtaining $D_e$ values using these solutions can be performed.
3. Fitting in the frequency domain

Parameter fitting in the frequency domain is performed by transferring experimental data to the frequency domain using the Fourier transform and comparing it to the LT solution for the process evaluated at values of s that allow comparisons between Fourier and Laplace transforms. The comparisons may be performed at a set number of discrete frequencies and parameter determinations then performed by minimizing the error between the model and the data. Although the transforms of the data, which are in the complex number domain, may be compared by more than one way (Anderssen and White, 1970, and Gangwal et al., 1971) the procedure used by Hays et al. (1967) and Clements (1969) is equivalent to minimizing the sum-of-squares error in the time domain between the experimental data and the model. This procedure is used and described in the Theory section of this work.

An advantage of this procedure is when the LT solution of a set of equations can be obtained, but an analytical solution in the time domain has not yet been obtained. In this case, the sum-of-squares error in the time domain can still be calculated without having the analytical, time domain solution. The FFT is a very efficient procedure used to transform discrete data to and from the frequency domain and experimental data are transformed at fixed frequencies which are determined by the number of data points in the data set and the total time interval of data collection. The relationship between the LT and the FFT, as shown in the Theory section, allows the inversion of the LT model from the frequency to the time domain and comparison
between the experimental data and the model may be visualized.

A disadvantage of parameter determinations in the frequency domain is that parameter optimization routines require function evaluations of the LT solution to estimate derivatives of the functions and that a significant number of function calls may be needed. Since for each LT function evaluation, the function must be evaluated at all frequencies of the transform, computational efforts may become relatively large when a large number of data points are used. The IMSL (1982) function minimization routine ZXMIN was used in this work for minimizing the error between the model and the experimental data. The bulk of the computation time for determining the model parameters in this study was spent evaluating the LT solution to the model at the frequencies required by the FFT; however, the advantage of this procedure over the method of moments is that the parameter values determined in this study were less sensitive to noise and drift in the tail of the response curves obtained.

4. Transfer function fitting

Transfer function fitting is where the LT solution, or transfer function, for a process is evaluated at discrete values of the LT variable, s, and compared to the experimental data transformed numerically to the LT domain using the definition of the LT. This procedure may be done for several values of s, but some rational choice of these s values must be made. Ostergaard and Michelsen (1969) have applied this procedure to parameter determinations for the plug flow dispersion model and Hopkins et al. (1969), and Michelsen and
Ostergaard (1970) examine the optimum size range of $s$ to be used. The advantage of this procedure is that the tail of the response curve is not weighted as heavily as it was in the moment method and requires less computational effort than fitting in the frequency or time domain; the disadvantage is having to justify the choice of $s$ used for the computations. As with weighted moments, different values of the weighting parameter weight different parts of the response curve unequally, and consistent procedures for determining the optimum values of the weighting factor are not developed or even desired since other procedures may be used.
III. THEORY

A. Definitions and Relations

1. Moments and the Laplace transform

Moments, or statistical moments, are a set of descriptive constants of a distribution which are useful for measuring its properties: they are defined as an integral of a distribution function. For \( C(t) \), the \( n^{th} \) moment, absolute moment, and central moment about the mean, are \( m_n \), \( \mu_n \), and \( \mu_n' \), respectively, and are related, as shown by Kendall and Stuart (1977), by

\[
m_n = \int_0^\infty C(t)t^n \, dt, \tag{37}
\]

\[
\mu_n = \frac{m_n}{m_0}, \quad \text{and} \quad \mu_n' = \frac{1}{m_0} \int_0^\infty C(t)(t - \mu_1)^n \, dt = \sum_{j=0}^{n} \frac{n!}{k!(n-k)!} \mu_{n-j}(-\mu_1)^j. \tag{39}
\]

Similar definitions exist for moments weighted with the weighting factor \( \exp(-pt) \). These moments will be referred to as weighted moments and they are defined by

\[
m_n(p) = \int_0^\infty C(t)\exp(-pt)t^n \, dt, \tag{40}
\]

\[
\mu_n(p) = \frac{m_n(p)}{m_0(p)}, \quad \text{and} \quad \mu_n'(p) = \frac{1}{m_0(p)} \int_0^\infty C(t)\exp(-pt)(t - \mu_1(p))^n \, dt. \tag{42}
\]
Moments of $C(t)$ can be related to the LT of $C(t)$. The definition of the LT is given by

$$\text{LT}[C(t)] = \overline{C}(s) = \int_{0}^{\infty} C(t) \exp(-st) \, dt, \quad (43)$$

and is equal to $m_0(p)$ evaluated at $p = s$. The relationship between weighted moments and the transfer function for a system are shown in Wakao and Kaguei (1982). The inverse LT is given by the Mellin inversion integral as

$$C(t) = \text{LT}^{-1}[\overline{C}(s)] = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{1}{s} \overline{C}(s) \exp(st) \, ds \quad (44)$$

where $\gamma$ is the exponential order of $C(t)$, and $\overline{C}(s)$ is related to moments by

$$m_n = (-1)^n \lim_{s \to 0} \frac{d^n \overline{C}(s)}{ds^n}, \quad \text{and by}$$

$$m_n(p) = (-1)^n \lim_{s \to p} \frac{d^n \overline{C}(s)}{ds^n}, \quad (45)$$

for weighted moments.

Moments of the LT solution of $C(t)$ for the lower chamber of a DWKDC will be subscripted with the letter L. Moments obtained using an impulse function, a square wave pulse, or bypass data will be subscripted with an I, S, or B, respectively. The moments that are not obtained using an impulse forcing function are related to the moments obtained when using an impulse function by
\[ \mu_{1LS} = \mu_{1LI} + \frac{t_{\text{inj}}}{2}, \quad (47) \]
\[ \mu_{2LS} = \mu_{2LI} + \frac{t_{\text{inj}}^2}{12}, \quad (48) \]
\[ \mu_{1LB} = \mu_{1LI} + \int_0^\infty F(t)tdt \int_0^\infty F(t)dt, \quad (49) \]
\[ \mu_{2LB} = \mu_{2LI} + \int_0^\infty F(t) (t - \mu_{1LB} - \mu_{1LI})^2 dt \int_0^\infty F(t)dt. \quad (50) \]

The second absolute moments can be calculated from
\[ \mu_{2LS} = \mu_{2LS} + \mu_{1LS}^2, \quad (51) \]
\[ \mu_{2LB} = \mu_{2LB} + \mu_{1LB}^2. \quad (52) \]

Subscripts will be deleted from the moments when their meaning is clear in the context in which they are used. The modifying terms "absolute" and "central moment about the mean" will not be specified when talking about moments in general terms.

2. The Laplace, Fourier, and discrete Fourier transforms

The fast Fourier transform, FFT, is just a very efficient method of calculating the discrete Fourier transform, DFT, of \( C(t) \). The DFT of a set of \( N \) equally spaced data points with time spacing \( \Delta t \), and its inversion formula, are given by (Brigham, 1974)

\[ \overline{C}(f_k = k/T) = \text{DFT}[C(t)] = \sum_{j=0}^{N-1} C(j\Delta t)\exp(2\pi jk/N), \quad (53) \]
\[
C(k\Delta t) = \text{DFT}^{-1}[\bar{C}(f_k)] = \frac{1}{N} \sum_{j=0}^{N-1} \bar{C}(f_j) \exp(-2\pi ijk/N), \quad (54)
\]

for \(k=0,1,2,\ldots,N-1\), \(i = \sqrt{-1}\) and \(T = N\Delta t\). The DFT approximates the integral

\[
\bar{C}(f_k) \cong \int_0^N C(j\Delta t) \exp(2\pi ijk/N) dj. \quad (55)
\]

If the function \(C(t)\) is zero outside the interval \([0,T]\), the LT, the Fourier transform, FT, and the DFT are related by

\[
\text{LT}[C(t)] = \bar{C}(s) = \int_0^T C(t) \exp(-st) dt, \quad (56)
\]

\[
\bar{C}(w) = \int_0^T C(t) \exp(2\pi iwt) dt, \quad (57)
\]

\[
= \Delta t \sum_{j=0}^{N-1} C(j\Delta t) \exp(2\pi ij\omega \Delta t) \Delta t, \quad (58)
\]

\[
\bar{C}(f_k) = \Delta t \sum_{j=0}^{N-1} C(j\Delta t) \exp(2\pi ijk/N). \quad (59)
\]

when \(s = -2\pi ik/T\) and \(w = f_k = k/T\) for \(k=0,1,2,\ldots,N/2\). For \(k > N/2\), the LT of a function does not agree with this definition of the DFT due to the symmetry relation of the DFT for a real sequence. The symmetry of the transforms dictates

\[
\bar{C}(f_k) = (N+2-k)/T = \bar{C}^*(f_{N-1-k}/T), \quad \text{for } k = 2,3,4,\ldots,N/2, \quad (60)
\]

where \(*\) denotes conjugation.
B. Composite Media Dynamic Wicke-Kallenbach Diffusion Cell Model

Originally the model used for diffusion, without adsorption, in the DWKDC was based on the equations presented by Burghardt and Smith (1979) with the impulse function replaced by the general forcing function, \( F(t) \). Experimentally, it was discovered that the calculated value of \( D_e \) decreases as the distance between the tracer dispersion cone and the pellet increased. It was conjectured that this decrease was the result of incomplete mixing in the upper chamber volume of the diffusion cell and that stagnant pockets of gas were present.

To try and model the effect of incomplete mixing in the upper chamber, the upper chamber volume, less the cone volume contribution, was broken-up into two parts. The upper part of the region was a region of ideal mixing. The second part was a region of stagnant gas and mass transfer through this region, from the well-mixed part to the top face of the pellet, occurred by bulk diffusion. The quantity "FRACTM" is defined as the fraction of upper chamber volume, less the cone volume, that is well-mixed, and varies from 0 to 1.

The extension of the equations given by Burghardt and Smith (1979), to include the two regions of different porosities and diffusivities was straight-forward; although, the algebra became tedious. The differential equations used to model the problem are

\[
V \frac{\partial C}{\partial t} = F U F(t) - F U C + AD \frac{\partial C}{\partial x} \bigg|_{x=0}, \tag{61}
\]

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} = \lambda \frac{\partial^2 C}{\partial x^2}, \quad 0 < x < L_1 \tag{62}
\]
\[
\frac{\partial C_2}{\partial t} = \frac{D_2}{\varepsilon_2} \frac{\partial^2 C_2}{\partial x^2} = \lambda_2 \frac{\partial^2 C_2}{\partial x^2}, \quad \text{and} \quad L_1 < x < L_2
\]  \hspace*{1cm} (63) 

\[
\nu \frac{\partial C_L}{\partial t} = -F_L C_L - AD_2 \frac{\partial C_2}{\partial x} \bigg|_{x=L_2}, \hspace*{1cm} (64)
\]

where \( L_1 \) = distance between the well-mixed chamber and the top of the pellet,
\( L_2 \) = distance between the well-mixed chamber and the bottom of the pellet,
\( \lambda_1 = D_1/\varepsilon_1 \), and
\( \lambda_2 = D_2/\varepsilon_2 \).

The subscripts refer to properties in media 1, the stagnant gas region, and media 2, the pellet. For media 1, \( \varepsilon_1 = 1 \), but the variable is left in the equation for generality. For media 2, \( D_2 = D_\varepsilon \) and \( \varepsilon_2 = \varepsilon_p \). The length of the pellet is \( L_2 - L_1 \) and for \( L_1 = 0 \), the problem reduces to that of Burghardt and Smith (1979) for \( F(t) = \mu \delta(t) \).

The boundary conditions used are

\[
C_1 = C_U \quad \text{at} \quad x = 0, \hspace*{2cm} (65)
\]

\[
C_1 = C_2 \quad \text{at} \quad x = L_1, \hspace*{2cm} (66)
\]

\[
-D_1 \frac{\partial C_1}{\partial x} = -D_2 \frac{\partial C_2}{\partial x} \quad \text{at} \quad x = L_1 \text{, and} \hspace*{2cm} (67)
\]

\[
C_2 = C_L \quad \text{at} \quad x = L_2, \hspace*{2cm} (68)
\]

All concentrations in the system are assumed to be zero at time zero.
The problem formulation is similar to that done by Lee (1980) for diffusion in a double-layered catalyst pellet; although, the author neglects accumulation in the upper chamber by using $C_U = M_0 \delta(t)$.

Deviating slightly from the solution procedure outlined by Ozisik (1980, pp. 294-303) by using Laplace transforms, the solution to the problem is

$$
\bar{C}_1 = A_{1i} \phi_1(x) + B_{1i} \theta_1(x), \ i=1,2, \quad (69)
$$

$$
\phi_1(x) = \sinh(\psi_1 x), \ i=1,2, \quad \text{and} \quad (70)
$$

$$
\theta_1(x) = \cosh(\psi_1 x), \ i=1,2, \quad (71)
$$

where $\psi_1^2 = s/\lambda_1$ for $i=1,2$.

The solution procedure for obtaining $\bar{C}_L = \bar{C}_2(x=L_2)$ is outlined in Appendix A. An alternate form of the the equation for $\bar{C}_L$ that is used in the computer program in Appendix C is equivalent to

$$
\left[ \frac{\bar{C}_L}{F(s)} \right]^{-1} = \left[ P_1 C_{C_1} + C_{C_2}/P_1 \right] \sinh(M_1 P_1) + C_{C_3} \cosh(M_1 P_1), \quad (72)
$$

$$
CC_1 = \frac{[AM_0 (V_U Z^2 + F_U) \sinh(M_1 P_1) + (V_U F_U + V_U F_U) Z + F_U F_U] \cosh(M_1 P_1)]}{F_U M_2}, \quad (73)
$$

$$
CC_2 = \frac{[A_2 M_6 (V_U Z^2 + F_U) \sinh(M_1 P_1) + (M_2 Z) \cosh(M_1 P_1)]}{F_U M_2}, \quad \text{and} \quad (74)
$$

$$
CC_3 = \frac{[((V_U F_U + F_U) Z + (F_U F_U) \sinh(M_1 P_1) + [M_2 ((V_U + V_U) Z + (F_U + F_U) \cosh(M_1 P_1)])}{F_U M_2}, \quad (75)
$$

where $M_1 = [L^2 \epsilon_2 s]^{1/2}$. \quad (76)
\[ M_2 = \frac{Ae_2}{\sqrt{2}}, \]  
(77)

\[ M_6 = \left[ D_1 e_1 \right]^{1/2}, \]  
(78)

\[ Z = \frac{1}{2}, \]  
(79)

\[ P_1 = \frac{1}{D_2}^{1/2}. \]  
(80)

C. Effective Diffusivity Calculations Using the FFT

1. Modification of experimental data

Experimental data were collected at a fixed sampling rate of 7.5 Hz and 256, 512, or 1024 data points were collected. These collected data sets contained noise and were subject to drift in the tail of the response curve. The modification of the data is to account for a non-zero baseline in the tail of the collected data. Baseline and zeroed trailing data values are obtained as described below. All data manipulations are performed by the computer program found in Appendix C.

The raw experimental data had the option of being smoothed using the cubic-interpolating, nine-point smoothing routine determined by Savitzky and Golay (1964). Smoothing of the complete data sets was not done since this had some influence on the value of \( D_e \) calculated.

To eliminate the non-zero baseline offset, the value of the last 50 data values of the data set were summed and the average value subtracted from all data values in the set to roughly establish a trailing baseline value of zero. After determining the peak maximum, the maximum value in the data set, a truncation point was determined. The truncation point is the point after which all trailing data values
are set to a value of zero.

In determining the truncation point, two of many options are available for use in the program. One procedure is to zero all the data values in the tail of the data set after reaching the first data value, or its average value determined by the nine-point smoothing routine, that is less than some selected percentage of the peak maximum value. Another option is to zero all trailing data values after a fixed collection time. The second procedure was chosen since the values of $D_e$ obtained using this procedure were less sensitive to noise and drift in the trailing data values. A different procedure was tried which was based on zeroing data values after a certain percentage of the area under the curve had been obtained. This procedure was extremely sensitive to drift in the tail of the response curve and was quickly abandoned.

After the truncation point was determined, all data values were shifted down by the average value of the truncation point, as determined by the nine-point smoothing routine. This prevented a sharp drop-off in the tail of the response curve and ensured a smooth transition to a zero baseline. The data values following the truncation point were zeroed as the data values in the leading edge of the response curve if they were less than zero, or, if the values increased and then decreased below the baseline. These fluctuations in the leading edge of the response curve were caused by a slight pressure differential sensed by the TCD when the pulse of tracer was injected into the diffusion cell.
At this point, the raw data have been modified and are ready for analysis. If fewer data values than were collected were desired for analysis, the number of data points was reduced by a factor of two by picking every-other data value. This was repeated until the desired number of points had been obtained. The value of the time spacing parameter, $\Delta t$, was increased accordingly. The entire procedure could also be applied to a data set obtained from a bypass experiment.

2. **Diffusivity calculation equations**

The minimization criteria used to determine the best fit between the experimental data and the model is equal to the unweighted sum-of-squares

$$SS_t = \sum_{k=0}^{N-1} [Y_e(t_k) - Y_m(t_k)]^2,$$

where $Y_e(t_k)$ and $Y_m(t_k)$ are the experimental values and the model results, respectively, evaluated at time $t_k = k\Delta t$. Using Parseval's theorem for the DFT (Brigham, 1974), equivalent sum-of-squares criteria in the frequency and the Laplace transform domains can be written as

$$SS_t = SS_f / N = SS_s / [N(\Delta t)^2],$$

where

$$SS_f = \sum_{j=0}^{N-1} \| \overline{Y}_e(f_j) - \overline{Y}_m(f_j) \|^2 = \sum_{j=0}^{N-1} (R_{f_j}^2 + I_{f_j}^2),$$

$$SS_s = R_{s0}^2 + I_{s0}^2 + 2 \sum_{j=0}^{N/2-1} (R_{s_j}^2 + I_{s_j}^2) + R_{sN/2}^2 + I_{sN/2}^2,$$

$$R_{f_j} = \text{Real}[\overline{Y}_e(f_j)] - \text{Real}[\overline{Y}_m(f_j)],$$

$$I_{f_j} = \text{Imag}[\overline{Y}_e(f_j)] - \text{Imag}[\overline{Y}_m(f_j)].$$
\[ I_{f_j} = \text{Imag}[\overline{Y_e}(f_j)] - \text{Imag}[\overline{Y_m}(f_j)], \quad (86) \]

\[ R_{s_j} = \text{Real}[\overline{Y_e}(s_j)] - \text{Real}[\overline{Y_m}(s_j)], \quad (87) \]

\[ I_{s_j} = \text{Imag}[\overline{Y_e}(s_j)] - \text{Imag}[\overline{Y_m}(s_j)], \quad (88) \]

\[ f_j = j/T, \quad j = 0,1,2,...,N-1, \text{ and } (89) \]

\[ s_j = -2\pi j/T, \quad j = 0,1,2,...,N/2. \quad (90) \]

The sum-of-squares computed in the program found in Appendix C is that shown in Equation (84).

The flow diagram in Figure 2 shows how the experimental data and the model are compared. The concentration of gas leaving the bottom of the diffusion cell is detected, amplified, and converted to discrete digital data. The discrete data are then converted to the frequency domain via the FFT and scaled by \( \Delta t \) to convert them to the LT domain. The model is evaluated at \( s = s_j \) and multiplied by a scale factor, \( SF \), to account for the scaling of the gas concentration by the TCD. The sum-of-squares is then calculated using Equation (84).

If the signal generated by the TCD is directly proportional to the gas concentration in the detector, then \( Y_e(t) \) and \( C_e(t) \) are related by

\[ Y_e(t) = \text{CON}_D \cdot C_e(t) \cdot \text{AMP}_D / \text{ATN}_D \quad (91) \]

where \( \text{AMP}_D \) = signal amplification for a dynamic run,

\( \text{ATN}_D \) = TCD attenuation for a dynamic run, and

\( \text{CON}_D \) = proportionality constant of TCD for a dynamic run.

For \( F(t) \) an impulse function or a square wave,
Figure 2. Flow diagram for comparison of experimental data to diffusion model.
\[ SF = M \frac{CON_D AMP_D}{ATN_D}. \]  

(92)

When \( F(t) \) uses the results of a bypass run,

\[ SF = \frac{CON_D ATN_B AMP_D}{(CON_B ATN_B AMP_B)}, \]  

(93)

where the subscript \( B \) applies for the bypass run. Since thermal conductivity detectors are very sensitive to changes in pressure and gas concentration, it was felt that the values of \( CON_D \) or \( CON_B \) determined in separate calibration experiments could not be used for all the runs performed. Another scaling procedure was used. The scaling used was

\[ SF = \Delta t \frac{\bar{Y}_e(f_j=0)}{\bar{C}_m(s_j=0)}. \]  

(94)

where \( \bar{C}_m \) is the concentration predicted by the model before scaling. This equates the areas of the experimental response curve and of the model's response curve.

The iteration parameters chosen to minimize Equation (84) were \( P_1 = 1 / (D_e)^{1/2} \), \( P_2 = t_{lag} \), and if a continuous square wave forcing function was used, \( P_3 = t_{inj} \). \( P_2 \) was allowed to vary to compensate for errors in estimating the lag-time. In the equation for \( \bar{C}_L \), \( D_2 = D_e \) is the only unknown. It was found that when working with the minimization procedure, it was easier to work with \( P_1 \) than with \( D_e \).

As with the method of moments, it was necessary to correct the model for the dead volumes between the GC valve and the top of the cell and between the bottom of the cell and the TCD. The lag-time correction, assuming plug-flow in the lines, for a dynamic run, \( t_{lagd} \),
is

\[ t_{\text{lagd}} = \frac{V_{\text{DU}}}{V_{\text{DL}}} / F_L, \quad (95) \]

where \( V_{\text{DU}} \) = upper dead volume, and \( V_{\text{DL}} \) = lower dead volume.

The terms \( V_U / F_U \) and \( V_L / F_L \) do not appear in the lag-time correction since they are already included in the modeling of the diffusion cell.

For the method of moments, the lag-time parameter, \( t_{\text{lagm}} \), is computed using

\[ t_{\text{lagm}} = t_{\text{lagd}} + t_{\text{inj}} / 2. \quad (96) \]

The expression used for the solution to the model, \( \bar{Y}_m(s_j) \), which includes the lag-time parameter \( P_2 \), is given by

\[ \bar{Y}_m(s_j) = SF\exp(-s_j P_2) \bar{C}_L, \quad (97) \]

where \( \bar{C}_L \) is obtained from Equation (72). Using this form for \( \bar{Y}_m(s_j) \) and Equation (41) for SF, the forcing function becomes normalized:

\[ \bar{F}(s_j) = \begin{cases} 1 & \text{impulse function,} \\ \left[1 - \exp(-s_j P_3)\right] / \left(s_j P_3\right) & \text{square wave function, and} \\ \Delta t \text{ DFT}[F(t)] \bigg|_{f_j=0}^T \int_0^T F(t)dt & \text{bypass function.} \\ \end{cases} \quad (98) \]

Initial estimates for \( P_2 \) were determined from Equation (95).

Initial estimates of \( D_e \) were obtained using the method of moments and were determined by solving \( \mu_{1L1} \) from Appendix A, with \( K_x = 0 \), for \( D_2 = D_e \). The corrected estimate of \( \mu_{1L1}, \mu_{1LC} \), obtained from the first
moment of the experimental data, $\mu_{ILE}$, is

$$\mu_{ILE} = \mu_{ILE} - t_{lagm}$$

and $D_e$ is given by

$$D_e = \left[ -A_2 + (A_2^2 - 4A_1A_3)^{1/2} \right] / [2A_1],$$

$$A_1 = \mu_{ILC} A(U_L + F_L) - A_2 L e_p - A(U_U + V_L),$$

$$A_2 = \mu_{ILC} L F_U F_L - A_2 L e_p (F_U + F_L) / 2 - L(U_U F_L + V_L F_U),$$

$$A_3 = -L^3 e_p F_U F_L / 6.$$  \tag{105}

When $P_3$ was used as an iteration parameter, $t_{inj}$ was first estimated using

$$t_{inj} = V_{inj} / F_U ,$$

and

$$V_{inj} = V_{GC} + V_{loop}$$  \tag{106}

where $V_{GC}$ = internal volume of GC valve, and

$$V_{loop} = \text{volume of sample loop.}$$

The value obtained for $V_{GC}$, by the filling and weighing of mercury, was $0.198 \times 10^{-6}$ m$^3$. Since $V_{GC}$ is small relative to $V_{loop}$, the size of the injected sample will be usually referred to by the size of the sample loop.

The volume of the upper chamber is calculated using

$$V_U = V_{cone} + (L_{VV}) \pi D_{ring}^2 / 4$$  \tag{108}

where $L_{VV} = L_{ring} - L - L_{cone}$, height of cone above pellet,
\[ L_{\text{ring}} = \text{length of pellet holding ring, and} \]
\[ L_{\text{cone}} = \text{depth of cone into ring.} \]

The fractional length of \( L_{VU} \) for ideal mixing, \( L_{VUM} \), and the fractional length of \( L_{VU} \) for gas diffusion, \( L_{VUD} \), are given by

\[ L_{VUM} = (FRACTM)L_{VU} \tag{109} \]
\[ L_{VUD} = (1-FRACTM)L_{VU} \tag{110} \]

From these relationships,

\[ L_1 = L_{VUD}, \text{ and} \tag{111} \]
\[ L_2 = L_1 + L. \tag{112} \]

D. Diffusion in Capillaries and Procedures for Calculating Tortuosities

In general, the pore structure and diffusion path of a species as it moves through a porous solid is complex and not well defined. Although models that can predict fluxes of gases through porous media, based on measurable properties of the particles such as porosity and pore size distribution, are desired, no comprehensive models exist. To circumvent this problem, some models include an adjustable parameter, the tortuosity factor, \( \tau \). \( \tau \) can be defined as the distance of the actual diffusion path divided by the distance of the straight line path for diffusion through a porous network. Before diffusion in a porous network can be discussed, an understanding of diffusion in capillaries is necessary.
1. Diffusion in capillaries

Diffusion in capillaries has been discussed elsewhere in the literature (Youngquist, 1970, and Satterfield, 1981) and only a brief review will be presented. For uniform pressure in a capillary, diffusion can occur either by molecular diffusion or by Knudsen diffusion. Knudsen diffusion occurs when the radius of the capillary is of the same order of magnitude as the mean-free path length of the diffusing molecules. A transition region is defined when both mechanisms for diffusion are present: this occurs when the pore-radius-to-mean-free-path ratio ranges from 0.1 to 10.

The flux of diffusing gas A, in a binary system A-B, is given by

\[ N_A = -D_T(r) \frac{dC_A}{dx} \]  \hspace{1cm} (113)

where \( N_A \) = flux of A, \( C_A \) = concentration of A, and

\[ D_T(r) \] is the total diffusion coefficient and is given by

\[ D_T(r) = \frac{1}{1 - \alpha y_A} \left( \frac{1}{D_{AB}} + \frac{1}{D_{KA}(r)} \right) \]  \hspace{1cm} (114)

where \( \alpha = 1 - (M_A/M_B)^{1/2} = 1 + N_A/N_B \),

\( N_B \) = flux of B,

\( D_{AB} \) = binary diffusion coefficient,

\( y_A \) = mole fraction of A, and

\( D_{KA}(r) \) is the Knudsen diffusivity of A and is given by
where $r$ is the pore radius. $D_{AB}$ can be obtained from experimental data or from the Chapman-Enskog equation (Dogu, 1986, pp. 436-439).

2. Procedures for calculating tortuosities

Since the flux $N_A$ is based on the cross-sectional area of a capillary and the effective flux in the porous solid is based on a cross-sectional area of the porous solid, some adjustments are needed to relate the two fluxes. In porous solids, it is assumed that the ratio of the open pore area to the total area at any cross-section of the pellet may be taken equal to the void-volume-to-total-volume ratio: the porosity. To account for the solid portion of the particle and the tortuous diffusion path the diffusing molecules encounter, the effective flux is related to $N_A$ by

$$N_{Ae} = \frac{e}{\tau} N_A$$

where $N_{Ae}$ is the effective flux through the porous solid. Using this relationship, $D_e$ is related to $D_T(r)$ by

$$D_e = \frac{e}{\tau} D_T(r)$$

Equation (117) is used to calculate $\tau$ for a particular system using experimental $D_e$ values after evaluating $D_T(r)$ at some pore radius. For a narrow pore size distribution, an average cylindrical pore radius, $r_{cyl}$, can be calculated from a void-volume-to-surface-area ratio using
\[ r_{cyl} = 2 \frac{V_p}{S_g} \]  

where \( V_p \) = pore volume, and 

\[ S_g = \text{pore surface area}. \]  

When mercury porosimetry is used to obtain pore size distributions, \( dV/dr \), the radius at which the distribution has its largest value is designated \( r_{\text{mode}} \) and this value can be used in the evaluation of \( D_T(r) \). A volume-averaged pore radius, \( r_{\text{mean}} \), can be calculated from the mercury porosimetry pore size distribution using 

\[ r_{\text{mean}} = \frac{\int_{r_{\text{min}}}^{r_{\text{max}}} r (dV/dr) dr}{\int_{r_{\text{min}}}^{r_{\text{max}}} (dV/dr) dr} \]  

(119)

where \( r_{\text{min}} \) = minimum pore radius for intrusion, and \( r_{\text{max}} \) = maximum pore radius for intrusion. 

Wang and Smith (1983) summed-up the contributions for \( D_T(r) \) over all pore sizes and calculated \( \tau \) using 

\[ \tau_{DG} = \int_{0}^{\infty} D_T(r) f(r) dr \]  

(120)

where \( f(r)dr \) represents the void area in pores with radius \( r \) and \( r + dr \), per total pellet area. \( f(r) \) can be thought of as a porosity distribution function and is related to \( dV/dr \) by 

\[ f(r) = \frac{dV}{dr} \frac{\epsilon_p}{V_{\text{max}}} \]  

(121)

where \( V_{\text{max}} \) is the maximum volume of mercury intruded into the sample.
Wang and Smith (1983) examine a variety of ways of calculating tortuosities and compare the $\tau$ values obtained using the different procedures.

Some of the following workers have developed models to predict tortuosity factors. Abbasi et al. (1983) performed Monte Carlo simulations for the diffusion of gas molecules in porous solids. For Knudsen diffusion, and for bulk diffusion, they obtained correlations for $\tau$ with respect to porosity and with ratio between the mean and the standard deviation of the pore size distribution. Wakao and Smith (1962) developed the random pore model and for monodispersed pore sizes, $\tau$ reduces to $\varepsilon_\text{p}^{-1}$. Feng and Stewart (1973) develop a model where, for an isotropic pore structure with no dead-ended pores, $\tau = 3$. Wheeler (1955) proposed a parallel pore model where he defined what is considered to be the tortuosity a value equal to $\sqrt{2}$, but for relating $N_{\text{Ae}}$ to $N_A$, $\tau$ would be equal to $(\sqrt{2})^2 = 2$.

Satterfield (1981, pp. 33-77) presents some values of $\tau$ determined experimentally and the values range roughly between 1.3 and 7.5 with values greater than 10 also being reported. Tortuosities calculated using Equations (117) through (121) should lie within these bounds.
IV. EXPERIMENTAL EQUIPMENT AND MATERIALS

A. Diffusion Apparatus

1. Dynamic Wicke-Kallenbach diffusion cell and flow apparatus

   a. Diffusion cell  A schematic drawing of the diffusion cell used is shown in Figure 3. The main components of the cell are the upper and lower parts of the cell, a pellet holding ring, and the tracer dispersion cone. Detailed drawings of the diffusion cell, a pellet holding ring, and cones A and B, are presented in Appendix B.

   The cylindrical rings used to hold the pellets have an I.D., \( D_{\text{ring}} \), of 25.4 mm and an O.D. of 38.0 mm. The length of a ring, \( L_{\text{ring}} \), varied and lengths of 10.80, 20.03, 22.22, 30.02, and 40.06 mm were used. The bottom of the ring was flat while the top of the ring had a square groove cut into it to allow an O-ring to fit between the top of the cell and the ring. A similar groove was cut into the top part of the diffusion cell. Rubber O-rings with a 30.2 mm (1-3/16") I.D. and a 0.938 mm (3/32") thickness were used to seal the ring between the upper and lower parts of the cell. Four machine screws were used to join the two parts of the cell.

   b. Flow apparatus  A sketch of the flow apparatus is shown in Figure 4. For all the diffusion experiments, 99.995% pure \( \text{N}_2 \) was used as the carrier and reference gas and \( \text{He}/\text{N}_2 \) mixtures of 9.86, 52.5, and 99.995% He were used as the tracer/diffusing gas. Separate cylinders of \( \text{N}_2 \) were used for the top and bottom flows to the cell and for the reference flow to the thermal conductivity detector (TCD). In Figure 4, valves T5, T6, and T7 would be in positions A: this was done to
Figure 3. Schematic diagram of diffusion cell
Figure 4. Schematic diagram of Old Apparatus
minimize pressure fluctuations that might be sensed by the TCD when a sample was injected into the upper chamber of the diffusion cell, even though the flow from the bottom of the cell is the monitored response.

The flow apparatus consists of gas cylinders fitted with pressure regulators, a sample loop connected to a six-port gas chromatograph (GC) sample injection valve, the stainless steel diffusion cell, a Gow-Mac Series 500 TCD, pressure gauges, a water filled manometer, and rotameters followed by soap-bubble flow meters. The analog output from the TCD was amplified by a Quasitronics, Inc. SA-1 Signal Amplifier, converted to a digital signal at a rate of 7.5 Hz by a Quasitronics, Inc. Q-3024 Analog-Serial Interface, and collected by a Perkin-Elmer 7500 Computer. Simultaneous strip chart recordings were made using a Fisher Scientific, Inc. Series 500 recorder operating at a speed of 100 or 200 mm/min.

c. Old Apparatus, New A, New B, and New C descriptions

Four modifications of the diffusion cell and flow apparatus were used for diffusion experiments. Except for the noted changes, the diffusion cell was used as shown in Appendix B. Unless stated otherwise, tracer dispersion cone A was used for all the diffusion experiments.

The diffusion cell shown in Appendix B and the flow apparatus shown in Figure 4 are referred to as the "Old Apparatus". The main distinction between the Old Apparatus and the other apparatus versions, that will be described shortly, is that the Old Apparatus contained the bypass valves T8 and T9. These valves were Whitey B-42XF 3-way ball valves which contained considerable dead space.
New Apparatus A, or New A, was a modification of the Old Apparatus. Bypass valves T8, T9, and the bypass loop were removed from the Old Apparatus. The tubing lengths between the diffusion cell and the TCD were shortened. Also, metering valves M1 and M4 were removed since they were not used to regulate flow through their lines. The volume of cone A was reduced to zero by filling the cone with DAP® '33' Glazing. The flow apparatus for New A, New B, and New C, is shown in Figure 5.

New B differed from New A only by its reduced lower chamber volume, $V_L$. For New B, the depression machined into the bottom part of the diffusion cell was filled with paraffin. The only volume contribution to $V_L$ was the space between the lower face of the pellet and the paraffin occupied by the compressed O-ring.

New C was a modification of New B which allowed the splitting of the flow from the bottom of the diffusion cell. For split flows, the tubing leading from the bottom of the diffusion cell to the TCD was cut and a Swagelok® SS-1F0-3GC GC union tee was installed. The volume of the tubing leading from the cell to the tee is referred to as $V_{DL}$ in the program found in Appendix C, and the volume of tubing from the tee to the TCD, $V_{DLTCD}$, is referred to a $V_{DLTCD}$ in the program. Another metering valve, M9, and rotameter/soap-bubble flow meter combination were added to the third leg of the tee. Additional drierite columns and fittings were added so the different tracer gas cylinders did not need to be disconnected and re-connected when using different tracer gas concentrations.
Figure 5. Schematic diagram of New Apparatus A, B, and C

D = Drierite column
M = Metering valve
R = Rotameter
S = Shut-off valve
T = Two-way valve
PG = Pressure gauge

He/N₂ MIXTURES
FOR NEW C ONLY
d. Apparatus volumes

The apparatus volumes are summarized in Table 1. The volumes of Cone A, the sample loop volumes, $V_{\text{loop}}$, and $V_L$ for the Old Apparatus were determined by the filling and weighing of mercury that filled those volumes. $V_{\text{cone}}$ for cone A has a volume of $0.901 \times 10^{-6}$ m$^3$ and sample loop volumes of $0.15 \times 10^{-6}$, $0.50 \times 10^{-6}$, $0.61 \times 10^{-6}$, $1.90 \times 10^{-6}$, and $5.21 \times 10^{-6}$ m$^3$ were used. $V_L$ was estimated to be $2.004 \times 10^{-6}$ m$^3$.

Dead volumes $V_{DU}$ and $V_{DL}$ for the Old Apparatus were determined using a combination of mercury fillings and weighings and estimating tubing volumes based on internal tubing diameters and lengths. The estimates of $V_{DU}$ and $V_{DL}$ for New A, New B, and New C are considered low estimates since these volumes were based on geometric calculations. Mercury fillings and weighings were not done due to the damaging effects mercury had on the brass fittings.

$V_L$ for New B and New C was taken as the space left by the bottom O-ring in the cell. The I.D. of a partially flattened O-ring was approximately 29.5 mm. The height of the compressed O-ring was determined by measuring the distance between the top and the bottom of the diffusion cell with and without the bottom O-ring in the cell. The thickness was determined to be 0.80 mm which gave a value of $0.547 \times 10^{-6}$ m$^3$ for $V_L$.

When running experiments with Cone B, various holes which carried the upper gas flow into the upper chamber were plugged with glazing. One configuration was to allow only flow through the center hole of the cone. Another configuration was to allow gas to enter the upper
Table 1. Apparatus volumes

<table>
<thead>
<tr>
<th>Volume x 10^6, m^3</th>
<th>Old Cone A</th>
<th>New A Cone A</th>
<th>New B Cone A</th>
<th>New C Cone A</th>
<th>New C Cone B</th>
</tr>
</thead>
<tbody>
<tr>
<td>V_{BLoop}</td>
<td>0.191</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>V_{DU}</td>
<td>1.631^a</td>
<td>0.128</td>
<td>0.128</td>
<td>0.128</td>
<td>0.193^b</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.198^c</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.360^d</td>
</tr>
<tr>
<td>V_{Cone}</td>
<td>0.901</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000^e</td>
<td>0.000</td>
</tr>
<tr>
<td>V_{L}</td>
<td>2.004</td>
<td>2.004</td>
<td>0.547</td>
<td>0.547</td>
<td>0.547</td>
</tr>
<tr>
<td>V_{DL}</td>
<td>2.101^f</td>
<td>0.460</td>
<td>0.460</td>
<td>0.140</td>
<td>0.140</td>
</tr>
<tr>
<td>V_{DLTCD}</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.452</td>
<td>0.452</td>
</tr>
</tbody>
</table>

^aV_{DU} for the bypass run was 1.482 x 10^{-6} m^3 since the tube leading from valve T8 to the diffusion cell was bypassed.

^bTop flow only through center hole of the cone.

^cTop flow only through one side hole of the cone.

^dTop flow through all five holes in the cone.

^eSome experiments were performed with the glazing removed from the cone and a value of 9.01 x 10^{-6} m^3 was used.

^fV_{DL} for the bypass runs was assumed to be the same value for the bypass runs as it was for the dynamic runs even though V_{DL} for the dynamic runs included the volume of the fitting which joined valve T9 to the diffusion cell.
chamber through one of the holes near the perimeter of the cone. The third configuration was to remove all the glazing and allow gas to enter the upper chamber through all five holes. The different values of $V_{DU}$, based on geometric estimates for these configurations, are given in Table 1.

2. Experimental procedure

For the dynamic and bypass experiments, flow rates and pressures of gases in the sample loop, in the top and bottom flow streams for the diffusion cell, and in the bypass loop, are controlled by the valves shown in Figures 4 and 5. Valves T8 and T9, in the Old Apparatus, control the flow of the carrier gas streams through the cell, or through the bypass loop. The data acquisition procedure for a bypass run is the same as the procedure used for collecting data for a dynamic experiment.

For the flow of the tracer gas, the two-way valves T1, T2, T3, and T4 in Figures 4 and 5 were in the A positions so that the pressure of the gas near the sample loop could be monitored by pressure gauge PG1. For all the runs performed with the Old Apparatus, M1 was completely opened and the flow of the tracer through the sample loop was controlled by valve M5. The flow through the sample loop was between $1.0 \times 10^{-6}$ and $1.3 \times 10^{-6}$ m$^3$/s and the pressure read from gauge PG1 was between 167 kPa and 170 kPa (9.0 and 10.0 psig). For New A, New B, and New C, the flow through the loop was between $1.3 \times 10^{-6}$ and $2.0 \times 10^{-6}$ m$^3$/s and the pressure read from PG1 was between 151 kPa and 158 kPa (7.2 and 8.2 psig). For the diffusion cell operating at approximately 153 kPa
(7.5 psig), a sample loop pressure of 154 kPa (7.6 psig), as determined by the injection of $N_2$ samples, gave a minimum pressure fluctuation at the TCD.

For dynamic diffusion experiments, valves T5 through T9, for the Old Apparatus, and T5 through T7, for the New versions, were in positions A. By appropriate adjustment of metering valves M2, M3, M5, M6, and M9 when using New A, New B or New C, the pressure in the top and bottom of the cell, as well as the flows to the top and bottom of the cell and to the TCD, could be set to their desired values. The pressures in the cell were balanced and maintained between 148 and 156 kPa (6.7 and 8.0 psig) for all runs. After balancing the pressures in the cell, with the GC valve in the injection position, shut-off valves S1 through S4 were closed to isolate gauges PG2, PG3, and the manometer, from the diffusion cell.

For bypass experiments performed with the Old Apparatus, where the injected sample bypasses the diffusion cell, valves T8 and T9 were switched to positions B. Before the bypass runs were made, the bypass loop was replaced with a piece of tubing of equal length and diameter, cut in half and fitted with a tee connector attached to pressure gauge PG4. In this manner, the approximate positions of metering valves M3 and M6, for different flow rates through the bypass loop, could be determined so that a pressure of approximately 150 kPa (7 psig) was present in the bypass loop. Once the valve positions were determined, the original bypass loop was re-installed and the bypass runs were conducted. Although designated PG4, pressure gauge PG2 was actually
used when making the pressure measurements.

Before collecting experimental pulse-response data, the flows through the apparatus were established and the TCD allowed to warm-up to a detector temperature of approximately 70°C. During warm-up, the cell pressures were balanced and the flows re-adjusted. The TCD was deemed ready when a near zero, stable baseline was obtained from the A/D converter while the GC valve was in the injection position. When ready to start a run, the GC valve was turned to the filling position for a minimum of 30 seconds and the strip chart recorder started with the pens in their down positions. To start the run, the GC valve was turned to its injection position while simultaneously pressing a key on the computer keyboard to start the data acquisition program, and also pressing a remote event marker switch for activating the event marker pen of the strip chart recorder. After the predetermined number of data points had been collected, the data collection program stopped and the event marker switch was struck again to signal the end of the data collection. The recorder was stopped and the data collected by the computer stored on disk. All experiments were conducted at a room temperature of 23°C. Five experiments were performed at each set of operating conditions.

B. Material

1. ZnS crystal form and purity

Reagent grade ZnS powders, Lot Numbers 771955 and 743422 obtained from Fisher Scientific, were used in this study. A formula weight of 97.43 was given. X-ray diffraction patterns were used to confirm the
wurtzite, not the sphalerite, form of the powder. Slight impurities were detected and the manufacturer indicated the major impurity, in Lot Number 771955, was approximately 3 wt% BaSO$_4$. Barium analysis on samples of ZnS powders were performed by the Iowa State University Engineering Research Institute Analytical Services Laboratory. Analysis of a sample from Lot Number 771955 gave 1.73 wt% Ba, which corresponds to 2.94 wt% BaSO$_4$. Analysis on two samples of ZnS powders from Lot Number 743422 gave 0.62 and 0.63 wt% Ba which corresponds to 1.05 and 1.07 wt% BaSO$_4$, respectively.

2. Powder and pellet preparation
   a. Powder preparation  Powder samples of ZnS for use in BET and mercury porosimetry experiments were obtained by sifting the reagent powder through a #35 mesh screen. A sample of Lot Number 771955 was sifted using a mechanical sonic sifter, fitted with different size screens, and particles in the following size ranges were obtained: 10-45 µm, 45-75 µm, 75-210 µm, and 210 µm and larger.

   b. Pellet preparation  The pellet holding rings, the base support for the rings, and the plungers for pressing the pellets were made from AISIW1 water-hardening tool steel. The steel was drawn and water quenched to give a hardness of 60 on the Rockwell C-Scale. Hardened steel was chosen to reduce the wear on the rings and plungers which was caused by powder which was trapped between the plunger and the ring as the powders were compacted.

   Except for the isostatically pressed pellets, the pellets were pressed in what is called a single-action die. A single-action die
compacts the powder from only one direction, which in these pressings, was from the top of the pellet. Here, a ring was placed on a pellet pressing base, the powder added to the ring, and a plunger placed over the powder and pressed into the ring using a Carver Laboratory Press. The pellets were pressed slowly at first to allow trapped air to escape and were held at their final pressing force for a minimum of 30 seconds. To remove a pellet from the ring, the pellet pressing base was replaced with an oversized ring which would allow the pellet to be pressed out of its ring.

The force gauge on the Carver Laboratory Press indicated the press was capable of pressing forces ranging from 0 to 106.76 kN (0 to 24,000 lbf) and the gauge could be read to ±0.44 kN (100 lbf). Calibration of the press with a calibrated strain gauge indicated that the actual pressing force was 2.80 kN (630 lbf) less than the value read from the gauge on the press. For all pressed pellets, the corrected pressing force is the value reported.

The above described procedure for pellet pressing was used on the majority of the pellets used in this work and is termed as unlubricated pellet pressing. Before pressing an unlubricated pellet, the base, ring, and plunger were rinsed with acetone and wiped dry to prevent the powder from sticking to the base or the plunger.

The pellets isostatically pressed were first pressed, unlubricated, to a force of 1.65 kN (370 lbf) using the Carver Laboratory Press. The ring and pellet were then placed in a Trojans®, unlubricated, latex condom, the air removed with a syringe, and the end
of the condom twisted and tied-off with a rubber band. The non-pellet end, beyond the rubber band, was cut off with a razor blade and the pellet/ring/condom assembly placed into another condom and sealed as was done with the first condom.

The isostatic press used was manufactured by the Autoclave Engineers and has a pressure range of 0.101 to 345 MPa (0 to 50,000 psig) with divisions every 3.55 MPa (500 psig). The condom enclosed pellet was placed in the oil bath of the press and pressed to its desired pressure. The pellet was pressed at its final pressure for 1 - 2 minutes.

Before pressing the powder for what is called a lubricated pellet pressing, the ring and plunger were dipped into a solution of stearic acid dissolved in ethanol. After the ethanol had evaporated, the pellet was pressed using the same procedure as an unlubricated pressing with the omission of the acetone rinsing step.

A composite pellet is essentially pressing more than one sample of powder in the ring after the previous sample had been pressed to its final pressing force using the Carver Laboratory Press. The first sample of powder is pressed as an unlubricated pellet. The second sample of powder was then added to the ring and pressed to its final pressing force. This procedure was repeated until the desired length of pellet had been obtained.

The length of a pellet was measured at three points across the face of the pellet with a micrometer, to the nearest 0.01 mm, and an average length calculated. The geometric pellet porosity, $e_{pg}$, was
calculated using
\[
\varepsilon_p = 1 - \frac{\rho_{\text{pellet}}}{\rho_{\text{ZnS}}} = 1 - \frac{\text{mass of pellet}}{\rho_{\text{ZnS}} \pi L \frac{D_{\text{ring}}^2}{4}}
\]  \hspace{1cm} (122)

C. BET Apparatus

The apparatus used to determine a sample's surface area, \( S_g \), and isotherms was a volumetric apparatus manufactured by the Micromeritics Instrument Corp. Two models were used: Model 2100D and 2100E Physical Adsorption Analyzers. The main difference between the two models was the pressure display and virtually the same results were obtained when using either machine.

Sample tubes of internal volumes ranging from roughly 15 to 20x10^{-6} \text{ m}^3 were used and for most experiments and between 3x10^{-3} to 4x10^{-3} kg of sample were used. All experiments were performed at 77 K: the temperature of liquid nitrogen at atmospheric pressure. Dead volumes were determined using He and N\(_2\) was used for the adsorption experiments. Samples were outgassed at approximately 100°C for a minimum of 690 minutes.

D. Mercury Porosimetry

The apparatus used was a Quantachrome Model #SP-200 Serial #135 Mercury Porosimeter. The filling apparatus of the porosimeter allows a vacuum to be applied to the sample and allows determinations of intrusion pore sizes above 7 \mu m. After filling pore volumes up to atmospheric pressure, volume-pressure intrusion/extrusion data could be collected for the pressure ranges 0.101 - 9.38 MPa (0 - 1200 psig),
0.101 - 41.5 MPa (0 - 6000 psig), and 0.101 - 414 MPa (0 - 60,000 psig). A scan rate of 3 was used for the 0.101 - 9.38 MPa and the 0.101 - 41.5 MPa experiments while a scan rate of 4 was used for the 0.101 - 414 MPa experiments. After each intrusion/extrusion experiment, the volume-pressure data collected by the porosimeter was transferred to an Apple IIe computer and stored on disk. These data were then uploaded to the University's main frame computer for analysis. For all calculations, the density of mercury, $\rho_{\text{Hg}}$ was taken to be $13.541 \times 10^3$ kg/m$^3$, the surface tension of mercury, $\gamma_{\text{Hg}}$, was taken to be $480 \times 10^2$ dynes/m, and the value of the contact angle, $\theta_{\text{Hg}}$, was taken to be 140°.

Sample cells with maximum intrusion volumes of $0.500 \times 10^{-6}$ m$^3$ were used for all experiments. Powder samples had a spring of known volume inserted into the cell to maintain electrical contact with the base plate of the sample cell. The mass of powder samples ranged from $0.54 \times 10^{-3}$ to $0.70 \times 10^{-3}$ kg.

Most pellets used for the porosimeter experiments were made from the unlubricated pressing of $4.00 \times 10^{-3}$ kg of powder in a 10.80 mm tall ring. Two isostatically pressed pellets were analyzed to compare their pore size distributions to the distributions obtained for pellets pressed without lubricant using the single-action die. The prepared pellets were pressed out of their ring and broken by hand into pieces just small enough to fit into the sample cell. The mass of pellet samples ranged from $1.01 \times 10^{-3}$ to $2.65 \times 10^{-3}$ kg.
E. Sedigraph Experiments

The sedigraph used for particle size determinations, based on Stokes' settling law, was a Micromeritics Model 5000ET Sedigraph. The experiments were performed with the apparatus operating at 32°C. The apparatus settling rate was set using the value obtained from the following equation:

\[
\text{Rate(start \mu m)} = 211.80 \times 10^{-3} \times \frac{(\rho_{\text{ZnS}} - \rho_w)^2}{\mu_w} \times \text{multiplier},
\]

where \( \rho_{\text{ZnS}} \) = density of the ZnS particles,

\( \rho_w \) = density of water,

multiplier = value determined by maximum starting particle diameter, and

\( \mu_w \) = viscosity of water.

Picking the starting particle size as 50 \( \mu \text{m} \), the manufacture gave a value of 1.00 for the multiplier. Using an estimate of \( \rho_{\text{ZnS}} \) of 4.00 \( \times 10^3 \) kg/m\(^3\), \( \rho_w = 0.9951 \times 10^3 \) kg/m\(^3\), and \( \mu_w = 0.7679 \) mPa-sec, a settling rate of 829 was obtained and this value was used for all sedigraph experiments.

Approximately 0.38 \( \times 10^{-3} \) kg of ZnS were place in approximately 40 ml of distilled water. Three to six drops of a solution of Calgon\(^\circledR\) Water Softener, distilled water which had been saturated with Calgon\(^\circledR\) and filtered with #5 Whatman Qualitative Filter Paper, were added to the mixture to act as a surfactant. The samples were disrupted by one of three procedures. One procedure was to stir the mixture for short times, on the order of minutes, with a magnetic stirring bar. A second procedure was to stir the suspension for approximately 1 day with a
magnetic stirring bar. The final procedure was to disrupt the suspension with a Tekmar Sonic Disrupter, Model #TM 500, Series 6523, at a power setting of 1 for 10 minutes using a 12.7 mm (1/2") disrupter horn. Once the samples had been disrupted, the samples were pumped through the sample cell and the pumping halted once the settling experiment was started.

F. SEM and TEM Photography

A JSM-U3 Scanning Electron Microscope (SEM) was used for all SEM photographs. Samples of reagent grade ZnS were mounted on graphite studs using Polaron Instrument, Inc. Quick Dry Colloidal Graphite #1204. The samples were gold sputtered for two to five minutes using a Polaron Instrument, Inc. SEM Coating Unit E5100 operating at 22 kv and 20 mA. These settings gave a gold coating of roughly 15.4 nm/min.

SEM photographs were taken of ZnS samples and two different sets of calibration grids. The actual magnifications, determined from pictures of the calibration grids, ranged between 1.40 and 1.70 times larger than the magnification indicated on the instrument at magnifications of 15 kX, 30 kX, and 45 kX. Due to the discrepancies between the magnifications obtained for the different grids at different magnifications, a median value of 1.55 times the machine magnification was used to estimate the size of the ZnS particles.

A Hitachi Model HU-125 Transmission Electron Microscope (TEM) was used for high magnification photographs of the ZnS powders. A sample of reagent grade powder was ultrasonically dispersed in methanol. A 200 mesh copper TEM grid with a carbon film support was dipped into the
suspension, removed from the suspension, and allowed to dry before TEM photographs were taken.
V. RESULTS

A. ZnS Powder and Pellet Characterization

1. BET experiments

a. Surface areas  
A summary of the samples used in the BET experiments and their calculated surface areas can be found in Tables 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder #1, 2, 3, 6</td>
<td>Samples of Lot Number 771955 obtained from different bottles.</td>
</tr>
<tr>
<td>Powder #4</td>
<td>Particles, obtained from sonic sifting, with diameters between 10-45 μm.</td>
</tr>
<tr>
<td>Powder #5</td>
<td>Particles, obtained from sonic sifting, with diameters greater than 210 μm.</td>
</tr>
<tr>
<td>Powder #9</td>
<td>Powder pressed in ring, 0.001 kg per pressing, at 104 kN (23,370 lb) and then crushed.</td>
</tr>
<tr>
<td>Powder #10</td>
<td>Sample of Lot Number 743422.</td>
</tr>
<tr>
<td>Pellet #95, 96</td>
<td>Unlubricated pressing of 0.004 kg powder at 19.4 kN (4370 lb).</td>
</tr>
<tr>
<td>Pellet #103</td>
<td>Unlubricated pressing of 0.008 kg powder at 19.4 kN (4370 lb).</td>
</tr>
</tbody>
</table>

and 3, respectively. BET surface areas were calculated using the BET equation
Table 3. Summary of BET experiments performed at 77 K

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Machine model #</th>
<th>Lot #</th>
<th>Powder/ pellet</th>
<th>Analysis type</th>
<th>C_{BET}</th>
<th>S \times 10^{-3} (m^2/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2100D</td>
<td>771955</td>
<td>Powder #1</td>
<td>S</td>
<td>158</td>
<td>8.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Powder #2</td>
<td>S</td>
<td>247</td>
<td>8.07</td>
</tr>
<tr>
<td>2</td>
<td>2100D</td>
<td>771955</td>
<td>Pellet #95</td>
<td>D</td>
<td>208</td>
<td>7.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pellet #96</td>
<td>A</td>
<td>62</td>
<td>8.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pellet #103</td>
<td>A</td>
<td>64</td>
<td>8.45</td>
</tr>
<tr>
<td>3</td>
<td>2100D</td>
<td>771955</td>
<td>Powder #3</td>
<td>S</td>
<td>130</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pellet #95</td>
<td>D</td>
<td>164</td>
<td>7.55</td>
</tr>
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<td></td>
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<td></td>
<td>Pellet #96</td>
<td>S</td>
<td>78</td>
<td>8.61</td>
</tr>
<tr>
<td>5</td>
<td>2100E</td>
<td>771955</td>
<td>Powder #4</td>
<td>S</td>
<td>86</td>
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<tr>
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<td></td>
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<td>Powder #5</td>
<td>S</td>
<td>116</td>
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<td></td>
<td>Powder #6</td>
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<td>136</td>
<td>8.22</td>
</tr>
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<td>6</td>
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<td>771955</td>
<td>Powder #6</td>
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<td>89</td>
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<td></td>
<td></td>
<td></td>
<td>Pellet #95(^b)</td>
<td>S</td>
<td>75</td>
<td>8.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pellet #96(^b)</td>
<td>S</td>
<td>82</td>
<td>8.05</td>
</tr>
<tr>
<td>7</td>
<td>2100E</td>
<td>771955</td>
<td>Powder #6</td>
<td>D</td>
<td>91</td>
<td>8.26</td>
</tr>
<tr>
<td>9</td>
<td>2100E</td>
<td>771955</td>
<td>Powder #9</td>
<td>D</td>
<td>112</td>
<td>8.35</td>
</tr>
<tr>
<td>11</td>
<td>2100E</td>
<td>743422</td>
<td>Powder #10</td>
<td>S</td>
<td>196</td>
<td>9.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Powder #10</td>
<td>S</td>
<td>188</td>
<td>9.46</td>
</tr>
</tbody>
</table>

\(^a\)S - Surface area, A - adsorption isotherm, D - adsorption/desorption isotherms.

\(^b\)Pellets crushed to powder before analysis.
\[ \frac{x_p}{(1-x_p)V_a} = \frac{1}{V_m C_{BET}} + \frac{(C_{BET} - 1)}{V_m C_{BET}} x_p \]  

(124)

where \( x_p \) = relative pressure, \( P/P_s \),

\( V_a \) = volume of gas adsorbed at pressure \( P \),

\( V_m \) = volume of gas adsorbed when the entire adsorbing surface

is covered by a monolayer,

\( C_{BET} \) = BET equation constant, and

\( P_s \) = saturation pressure of the adsorbing gas.

Plotting \( x_p/(1-x_p)V_a \) versus \( x_p \) should give a straight line up to a

limiting value of \( x_p \) where the assumptions in the BET model break down.

For calculations, a Perfect Gas Correction Factor of 0.495 \((\mu Pa)^{-1}\), or

6.6x10\(^{-5}\) \((\text{mm Hg})^{-1}\), was used as was a value of the surface area

occupied by a \( N_2 \) molecule of 16.2x10\(^{-2}\) \(\text{nm}^2\). Vapor pressure values of

\( N_2 \) were obtained by linear interpolation between the values of

97.245 kPa and 103.228 kPa (729.398 and 774.270 mm Hg) at 77.0 and 77.5

K, respectively.

In the experiments performed, the BET equation plots had an upward

deviation from the straight line for \( x_p > 0.225 \). All surface areas

were calculated using linear regression on the data corresponding to \( x_p \)

\( \leq 0.225 \). The values of \( C_{BET} \), the constant in the BET equation, are

also included in Table 3 and lie between 62 and 247 for the samples

analyzed.

The average surface area for Lot Number 771955, averaging the

values for Powders #1, #2, #3, and #6, is 8.17x10\(^3\) \(\text{m}^2/\text{kg}\). For the two
experiments performed on powder samples from Lot Number 743422, an average area of \(9.43 \times 10^3\) m\(^2\)/kg was obtained and these average areas represent a difference of 15.4% between the surface areas of the two lot numbers analyzed. The difference in surface areas between the two lot numbers is greater than the difference in surface areas between two samples run on the same machine, BET experiments #1 and #9; two samples run on different machines, Powder #3 in BET experiment #3 and Powder #6 in BET experiment #5; two samples sifted to different particle sizes, Powders 4 and 5 in BET experiment #5; and the reagent powder and a powder prepared by pressing powder at a high pressing force and then crushing the powder, Powder #3 in BET experiment #3 and Powder #9 in BET experiment #9.

The discrepancies in the surface areas of Pellet #95, the surface area being smaller than the average powder surface area, and Pellet #96 having a surface area larger than the average surface area of the powder, could not be explained. The surface area measurements made in BET experiment #2 were repeated in BET experiment #3 and similar results were obtained. When the pellets were crushed into powders, in BET experiment #6, their surface areas were closer to the average surface area of the powders from the same Lot Number.

b. Isotherms and pore size designations

The adsorption/desorption isotherms for Powders #6 and #9 are shown in Figure 6. These are typical of what is referred to as a BDDT Type IV isotherm (Gregg and Sing, 1982, pp. 25-26). Previously, pore sizes had been divided into macropores and micropores and no distinction was made
Figure 6. BET nitrogen isotherm for Powders #6 and #9 at 77K
as to pore sizes these ranges included. Gregg and Sing (1982), have divided pore sizes into three different size ranges and and discuss the types of isotherms that are characterized by these different pore size ranges. Porous solids containing mesopores, pore sizes in the range of 2 to 50 nm, give rise to Type IV isotherms. The inability to reach a plateau at relatively high values of \( x_p \) indicate the presence of macropores: pore sizes greater than 50 nm. If micropores, pore sizes smaller than 2 nm, were present, larger values of \( C_{BET} \) and \( S_g \) would have been obtained. Pore size distributions in the mesopore and macropore size ranges are better obtained using mercury porosimetry. The absence of micropores and the presence of mesopores and macropores is supported by pore size distributions determined by mercury porosimetry experiments, which are discussed in the next section.

The desorption curve for a Type IV isotherm hysteresis loop should connect with the adsorption curve near \( x_p \) equal to 0.42 when using \( N_2 \) at 77 K (Gregg and Sing, 1982, pp. 154-155). The failure of the desorption curve to re-join with the adsorption leg of the isotherm is called low pressure hysteresis. Bailey et al. (1971), explain this phenomenon in terms of swelling and cracking of the particles during adsorption. The swelling distorts the structure and opens up cavities which were previously inaccessible to adsorbate molecules. The adsorbate is trapped in these cavities and the low pressure hysteresis curve is observed. Although this phenomenon may be important during a reaction, it does not present a problem for the diffusion measurements since the physical adsorption of \( N_2 \) on solids at room temperature is
quite small and the adsorption of He would be even smaller.

2. Mercury porosimetry experiments

Mercury porosimetry experiments were performed to determine pore size distributions of the powders and pellets. Table 4 summarizes the results obtained from various experiments. After filling pores of radii larger than 7 um, using a 0 to 101 kPa (0 - 1 atm) intrusion, a 0.101 - 41.5 MPa intrusion/extrusion experiment was performed, followed by a 0.101 to 414 MPa intrusion/extrusion experiment. Pore size distributions were calculated from the collected volume-pressure data obtained from the 0.101 - 41.5 MPa experiments since between 91 and 96% of the total mercury intruded was intruded at a pressure of 41.5 MPa. The 0.101 - 414 MPa experiments were performed to check for the presence of micropores and to determine total intruded volumes for porosity calculations. The pore size distributions obtained indicate pore sizes in the mesopore and macropore size ranges and these results support the contention of BET results that micropores are absent from the ZnS particles.

Some discoloration of the ZnS samples occurred during the mercury porosimetry experiments. The ZnS samples before mercury intrusion were white and appeared dull grey after the intrusion experiments. Initially, it was thought that some form of mercury sulfide was being formed during the experiments. X-ray diffraction patterns were taken on samples of Pellet #391 before and after mercury intrusion. When preparing the sample that had been in contact with the mercury for x-ray analysis, the grinding of the sample produced droplets of mercury.
Table 4. Summary of powder and pellets used in mercury porosimetry experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressing force (±0.44 kN)</th>
<th>L (mm)</th>
<th>$\varepsilon_{pg}$</th>
<th>$\varepsilon_{pm}$</th>
<th>$V_{max} \times 10^4$ (m$^3$/kg)</th>
<th>Pore radius $^b$ (nm)</th>
<th>$r_{mode}$</th>
<th>$r_{mean}$</th>
<th>$r_{cyl}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder #10</td>
<td>--</td>
<td>--</td>
<td>0.708</td>
<td>5.79</td>
<td>82.3</td>
<td>400.6</td>
<td>122.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pellet #395</td>
<td>1.65</td>
<td>4.35</td>
<td>0.556</td>
<td>0.547</td>
<td>2.92</td>
<td>69.3</td>
<td>90.4</td>
<td>61.9</td>
<td></td>
</tr>
<tr>
<td>Pellet #396</td>
<td>8.32</td>
<td>3.71</td>
<td>0.480</td>
<td>0.464</td>
<td>2.22</td>
<td>62.4</td>
<td>59.3</td>
<td>47.1</td>
<td></td>
</tr>
<tr>
<td>Pellet #399</td>
<td>19.44</td>
<td>3.45</td>
<td>0.436</td>
<td>0.422</td>
<td>1.80</td>
<td>43.8</td>
<td>46.2</td>
<td>38.2</td>
<td></td>
</tr>
<tr>
<td>Pellet #400</td>
<td>37.23</td>
<td>3.25</td>
<td>0.406</td>
<td>--</td>
<td>1.57$^c$</td>
<td>39.5</td>
<td>48.1</td>
<td>33.3</td>
<td></td>
</tr>
<tr>
<td>Pellet #392$^d$</td>
<td>43.67</td>
<td>3.20</td>
<td>0.396</td>
<td>0.380</td>
<td>1.55</td>
<td>38.1</td>
<td>37.5</td>
<td>32.9</td>
<td></td>
</tr>
<tr>
<td>Pellet #402</td>
<td>103.95</td>
<td>3.10</td>
<td>0.377</td>
<td>0.350</td>
<td>1.32</td>
<td>30.2</td>
<td>35.4</td>
<td>28.0</td>
<td></td>
</tr>
<tr>
<td>Pellet #391$^e$</td>
<td>105.68</td>
<td>3.00</td>
<td>0.357</td>
<td>0.345</td>
<td>1.30</td>
<td>29.5</td>
<td>33.6</td>
<td>27.6</td>
<td></td>
</tr>
</tbody>
</table>

$^a$From lot number 743422. Pellets #395, #396, #399, #400, and #402 obtained from the unlubricated pressing of 4.00 x 10$^{-3}$ kg of powder.

$^b$From intrusion data.

$^c$Estimated from a plot of $V_{max}$ versus $\varepsilon_{pm}$, evaluated at $\varepsilon_{pg} = 0.406$, since the 414 MPa intrusion malfunctioned.

$^d$Pressed isostatically, from 4.00 x 10$^{-3}$ kg of powder, at 12,500 ± 250 psig.

$^e$Pressed isostatically, from 4.00 x 10$^{-3}$ kg of powder, at 30,250 ± 250 psig.
The x-ray patterns for the two samples were the same except for a slight rise in the baseline of the x-ray pattern in the 2.056 to 2.795 d-spacing region for the mercury intruded sample. This discrepancy between the two diffraction patterns was attributed to the presence of adsorbed mercury on the sample and no further analysis of the intruded samples were performed.

Figure 7 shows the volume versus pressure intrusion/extrusion curves obtained for Pellet #399. The volume-pressure data were fitted with cubic splines and evaluated at equal pressure intervals. To avoid erroneous derivatives of the volume-pressure data, the nine-point smoothing routine, discussed in the Theory section, was used to smooth the data. The data for the reagent powder were smoothed twice to eliminate discontinuities in the volume data at low pressures while the volume-pressure data for the pellets were smoothed once.

The relationship used to relate pressure to pore radius was the Washburn equation (Lowell and Shields, 1984):

\[ P_{Hg} r = -2\gamma_{Hg} \cos \theta_{Hg} \] (125)

where \( P_{Hg} \) is the pressure difference between the mercury and the interior of the capillary. The pore size distribution function, \( dV/dr \), is related to derivatives of the volume-pressure data by

\[ \frac{dV}{dr} = \frac{dV}{dP_{Hg}} \frac{dP_{Hg}}{dr} = \frac{dV}{dP_{Hg}} \frac{P_{Hg}}{r} \] (126)

The values of \( dV/dP_{Hg} \) were determined using cubic spline coefficients fitted to the smoothed volume-pressure data and the values of \( r \) were
Figure 7. Volume versus pressure mercury porosimetry results for Pellet #399
determined from the Washburn equation.

Figure 8 shows \( dV/dr \) versus pressure obtained for intrusion/extrusion experiments performed on Pellet #399. The presence of the hysteresis loop shown in Figure 7 gives rise to the difference between the pore size distributions for the intrusion and extrusion experiments. The intrusion pore size distributions versus pore radius for the samples found in Table 4 are shown in Figure 9. The plots for Pellets #391 and #392 were not included since their distributions are quite similar to the distributions obtained for Pellets #400 and #402, respectively.

The values of \( r_{\text{mean}} \), listed in Table 4, were calculated from \( dV/dr \) using Equation (119). The average cylindrical pore radii, \( r_{\text{cyl}} \), listed in Table 4 were calculated using Equation (118) where \( V_p \) was taken equal to \( V_{\text{max}} \): the value of \( V \) at \( P_{\text{Hg}} \) equal to 414 MPa. The value used for \( S_g \) was 9.43x10^3 m^2/kg which is the average BET surface area of the two determinations performed on Powder #10.

3. Sedigraph experiments

To determine the strength of particle aggregates, sedigraph particle settling experiments were performed on ZnS suspensions that had been disrupted with different intensities. Experimental sedigraph results are given as cumulative mass% versus \( D_{\text{SED}} \), the equivalent spherical particle diameter.

Figure 10 shows the sedigraph results for a sample of Lot Number 771955 ZnS. As can be seen in the figure, the particle aggregates can be easily broken by the agitation of the suspension by a rotating
Figure 8. $dV/dr$ versus pressure mercury porosimetry results for Pellet #399
Figure 9. $dV/dr$ versus $r$ for mercury porosimetry intrusion experiments
Figure 10. Sedigraph results for sonically disrupted ZnS powders
magnetic stirring bar. The sonic disruption was believed to have broken up the aggregates into their primary particles.

Results similar to those shown in Figure 10 were obtained for a sample of powder from Lot Number 743422. Figure 11 shows the sedigraph results for ZnS samples from Lot Number 771955 and Lot Number 743422 after they had been sonically disrupted. The curve for the Lot Number 743422 powder lies above and to the right of the other curve which indicates that the primary particle from the Lot Number 743422 powder are smaller than the primary particles from Lot Number 771955. This result is consistent with BET surface area results where the powder from Lot Number 743422 had a higher surface area than the surface area of the Lot Number 771955 powder.

4. Average particle diameter

Many times it is desired to estimate an average particle diameter based on a BET surface area measurement. Assuming the particles are spherical and are all of the same diameter, the average particle diameter for Lot Number 743422 is given by

$$D_{\text{BET}} = \frac{6}{\rho \cdot S_g} = 0.156 \, \mu m$$

(127)

when using $\rho_{\text{ZnS}} = 4.087 \times 10^3 \, \text{kg/m}^3$ and $S_g = 9.43 \times 10^3 \, \text{m}^2/\text{kg}$.

In sedigraph settling experiments, a spherical particle shape is assumed and the results are given in terms of an equivalent spherical diameter. A common procedure is to equate the mean spherical particle diameter, $D_{\text{SED}}$, to the equivalent spherical particle diameter for cumulative wt\% of 50. Using this procedure for the powder that had
Figure 11. Sedigraph results for sonically disrupted ZnS samples from Lot #771955 and #743422.
undergone sonic disruption, $\bar{D}_{SED} = 0.31 \mu m$.

SEM and TEM photographs clearly show the non-spherical, irregular shape of the particles and the wide particle size distributions. Rough estimates of particle diameters determined from the SEM and TEM photographs give $\bar{D}_{SEM}$ between 0.07 and 0.24 $\mu m$ and $\bar{D}_{TEM}$ between 0.09 and 0.29 $\mu m$. These were only crude estimates of the particle sizes and the actual range of particle sizes may be larger. Image analysis of the photographs was not possible due to the large number of particles that were touching one another.

5. ZnS density determinations

The value of $\rho_{ZnS}$ for the wurtzite form, is given in Perry and Chilton (1973) as $4.087 \times 10^3$ kg/m$^3$. The value given in Weast (1976) is $3.98 \times 10^3$ kg/m$^3$. Density determinations performed with the BET apparatus on four powder samples gave an average value of $4.13 \times 10^3$ kg/m$^3$. Although the BET sample tube volumes were too small to give precise data, the agreement between the four samples was within 7% of one another. Density calculations from the mercury porosimetry experiments performed on the samples shown in Table 4 gave an average value of $4.05 \times 10^3$ kg/m$^3$ and an agreement within 8% of each other. Since these density data had some scatter about their mean values, it was decided to use the value given by Perry and Chilton (1973) for calculation purposes.

B. Diffusion Experiments

The descriptions of the pellets used for the diffusion experiments are summarized in Table 5. All the pellets in the table were pressed
from ZnS powder from Lot Number 743422. Preliminary pellet pressing studies showed that pellets pressed with the different lot number powders compacted differently. Powder from Lot Number 743422 was used for all diffusion experiments due to the lack of Lot Number 771955 powder available for sample preparation.

The number of data points collected for analysis was determined by the time required to obtain a stable baseline in the tail of the experimental response curve. For dynamic experiments, 256, 512, or 1024 data points were collected at a frequency of 7.5 Hz and any bypass run which was used as a forcing function for the dynamic runs contained the same number of data points. The last 50 data values were averaged to determine the value of the baseline shift and the data values following the truncation times of 33, 67, and 135 seconds, for 256, 512, and 1024 data points, respectively, were set to zero.

These trailing 50 data values averaged for the baseline calculations were chosen so that a sufficient number of points were collected so a long, smooth tail in the response curve was obtained. If the 50 data values reached into the decreasing portion of the response curve, the number of data points collected was increased. The choice of the truncation times were somewhat arbitrary, but were chosen as values near the end of the response curves. The choice of the truncation times did not affect the values of $D_e$ calculated by the FFT procedure as much as they did the values calculated using the moment method.

To reduce computation time, the number of points in a data set and
Table 5. Descriptions of pellets used for diffusion experiments

<table>
<thead>
<tr>
<th>Pellet</th>
<th>Mass ($\text{kg} \times 10^{-3}$)</th>
<th>$L_{\text{ring}}$ (mm)</th>
<th>Pressing force ($\pm 0.44 \text{kN}$)</th>
<th>$L$ (mm)</th>
<th>$\varepsilon_{\text{pg}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>4.00</td>
<td>10.80</td>
<td>19.44</td>
<td>3.43</td>
<td>0.437</td>
</tr>
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<td>501</td>
<td>4.00</td>
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<td>01.65</td>
<td>4.08</td>
<td>0.527</td>
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<td>10.80</td>
<td>37.23</td>
<td>3.25</td>
<td>0.406</td>
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<td>4.00</td>
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<td>30.02</td>
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<td>19.59</td>
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\(^a\) Pellet #513 was an aluminum SEM stub, with a 1.6 mm (1/16" hole drilled through the center, which was glued inside a ring.

\(^b\) Composite pellets pressed using $8.00 \times 10^{-3} \text{kg}$ per pressing.

\(^c\) Pellet #521 was a piece of Whatman #5 Qualitative Filter Paper glued to the bottom of a ring.
the sampling frequency were reduced by a factor of two until it was
determined that a minimum sampling frequency was reached. A minimum
sampling frequency was checked by one of two ways. The first was by
reducing the number of data points and the sampling frequency until
different values of $D_e$ were obtained using the FFT procedure. The
second way was to compare theoretical absolute moments to absolute
moments calculated by cubic splines fit to the model's FFT inverted
time domain values: cubic splines were computed using the IMSL (1982)
subroutine ICSICU with the end point second derivatives set to zero.
Agreement to three digits or more in the values of the absolute moments
implied a sufficiently fast sampling rate was used for data analysis.
For most cases, reducing the number of data points and the sampling
frequency by two gave the smallest acceptable sampling frequency.

Starting iteration values for the lag-time parameter, $P_2$ and $D_e$,
were calculated using Equation (95) and Equation (102), respectively.
For some conditions, these initial lag-time estimates were not close
enough to a solution to allow the IMSL (1982) ZMIN subroutine to
converge on a minimum sum-of-squares and different starting values were
tried until convergence was obtained.

Three to five of the runs performed at each set of operating
conditions were analyzed, using the FFT procedure and NSIG = 3 in the
ZMIN subroutine, and the $D_e$ values presented are averages of these
values. Unless stated otherwise, pulses of pure He were used in the
experiments and an impulse forcing function was used in the FFT model.
When presenting results with $F_U$ and $F_L$ approximately equal, an average
flow rate, $F_{ave} = (F_U + F_L)/2$, will be used.

For all versions of the experimental apparatus, the values of $D_e$ calculated, using the FFT procedure, were more consistent between repeated runs than the values calculated by the equating of theoretical and corrected experimental first moments. $D_e$ values calculated using the FFT were usually within 2% of one another for repeated runs at the same conditions and the difference increased to 6% as the detection limit of New C was approached. $D_e$ values from moments were close to one another at low flows, but the difference increased to over 25% for the repeated runs as signal noise and drift was encountered. First absolute moments and second central moments were consistent between one another for repeated runs at low flows, but the differences increased as noise and drift became relatively more important and negative values for the second central moments were not uncommon.

1. Old apparatus

An experimental response curve, Run #403, with $F_{ave} = 5.0 \times 10^{-6}$ m$^3$/sec and $V_{loop} = 0.50 \times 10^{-6}$ m$^3$, for Pellet #500, and the results of fitting the FFT model to the experimental data, are shown in Figure 12. The fitting procedure tends to shift the curve slightly as shown, but the match between the two curves appears quite good.

A series of experiments were performed on Pellet #500 using three procedures: (1) $F_U$ increasing for a fixed value of $F_L$, (2) $F_L$ increasing for a fixed value of $F_U$, and (3) $F_U$ and $F_L$ approximately equal and increasing, and these results are shown in Figure 13. Similar results were obtained for Pellets #501-503. The dependence of
Figure 12. Comparison between experimental response curve and FFT modeling results
Figure 13. Old Apparatus FFT $D_e$ results versus flow rate using different flow conditions.

Pellet #500  $V_{Loop} = 0.50 \times 10^{-6}$ m$^3$

$F_L = 6.25 \times 10^{-6}$ m$^3$/sec  
$F_U = 4.76 \times 10^{-6}$ m$/sec  
F_U = F_L$
De on upper and lower flow rates is apparent and the additive effect was shown for the case of \( F_U = F_L \).

It was found that the value of the truncation time used could affect the values of \( D_e \) calculated using the method of moments. Data from runs performed on Pellet #501 were analyzed using different truncation times. For this procedure, all 256 of the collected data points were used in the analysis.

\( D_e \) results using the method of moments and the FFT procedure for two runs with different flow rates, Runs #495 and #465 with \( F_{ave} = 2.05 \times 10^{-6} \) and \( 10.2 \times 10^{-6} \) m\(^3\)/sec, respectively, are presented in Figure 14. For the lower flow rate run, the effect of truncating the tail at different times is less pronounced for both methods of calculating \( D_e \) until the truncation point starts eliminating part of the trailing edge of the response curve. For truncation times less than 12 seconds, the \( D_e \) values increase greatly and are not plotted. On the other hand, \( D_e \) values calculated for the higher flow rate run using the method of moments are quite erratic while the values calculated using the FFT procedure are less sensitive to noise and dips in the tail of the response curve. The advantage of using the FFT over the method of moments when signal noise and drift is present, is obvious.

Bypass experiments were performed with the flow rates varying from \( 3.00 \times 10^{-6} \) m\(^3\)/sec to \( 10.0 \times 10^{-6} \) m\(^3\)/sec. Five runs at each flow rate were performed and 256 points collected; although, far fewer points were actually needed to represent a run since its response time was so short. Fifty points were used for the baseline shift and a truncation
Pellet #501  $V_{\text{Loop}} = 0.50 \times 10^{-6} \text{ m}^3$

Run #465  Moments  +
Run #465  FFT  □
Run #495  Moments  ◇
Run #495  FFT  X

Figure 14. $D_e$ versus truncation time for Runs #495 and #465
time of 12 seconds was used for all the bypass runs to reduce signal
noise and drift in the tail of the response curve. The use of the
experimental bypass results was as follows. The runs performed on
Pellet 500 with $F_U = F_L$ were chosen for analysis. The first run
performed at each flow rate was analyzed using the FFT procedure using
each of the five bypass runs. The values of $D_e$ calculated were
averaged and the bypass run that gave the $D_e$ value closest to the
average was used as the bypass run for analyzing the other dynamic runs
at the same flow rate. The five $D_e$ values determined this way were
averaged and this was the value reported at the particular flow rate.

The runs performed on Pellet #500 were also analyzed using the FFT
procedure with a square wave forcing function where $P_3$ was allowed to
vary. It was found that the value of $t_{inj}$ calculated from $V_{inj}$ and $F_U$
was not close enough to a solution to allow iterations to begin since
the Jacobian matrix was not positive-definite. Also, the value of $t_{lag}$
calculated from dead volumes and flows had to be greatly decreased
before iterations would proceed. The values of $D_e$ calculated for
Pellet #500 using the method of moments, the FFT procedure with the
forcing function being an impulse, an ideal square wave, or bypass data
forcing function, are shown versus $F_{ave}$ in Figure 15. The sum-of-
squares errors calculated when using the different forcing functions
gave the largest error for the impulse function and the smallest error
for the square wave function. It was determined that iterating on the
value of $P_3$ reduced the sum-of-square error, but the value obtained did
not have any physical significance.
Figure 15. Old Apparatus FFT $D_e$ results versus $F_{ave}$ using different forcing functions

Pellet #500 $V_{Loop} = 0.50 \times 10^{-6} \, m^3$

- Impulse
- Square wave
- Bypass
- Moments
The variation of $D_e$, calculated using the FFT procedure, with $L$ is shown in Figure 16. As $L$ increases, $D_e$ increases. The experimental response curves for the different length pellets at $F_{ave} = 3.00 \times 10^{-6}$ m$^3$/sec are shown in Figure 17. As can be seen in the figure, the experimental response curves are similar to one another. The explanation for $D_e$ increasing with increasing $L$, for similarly shaped response curves, can be found in the Discussion section.

2. New A

As seen in Figure 17, the different length pellets have a small effect on the experimentally measured response curves. It was decided that the dead volumes in the bypass valves and apparatus tubing were major contributors to the spread of the response curve and that the changes described earlier, the changes applied to the Old Apparatus to convert it to New A, would reduce these dead volume contributions.

The $D_e$ results comparing the New A results to the Old Apparatus results are shown in Figure 18. All New A results are from using a $0.61 \times 10^{-6}$ m$^3$ sample loop and the Old Apparatus results are from using a $0.50 \times 10^{-6}$ m$^3$ sample loop. It is shown later that this small difference in sample loop volumes has virtually no effect on the value of $D_e$ calculated. As can be seen, the New A results give larger $D_e$ values than the Old Apparatus results. This would be expected since the spread of the response curves was reduced and a larger $D_e$ value would be determined by the FFT procedure.
Figure 16. Old Apparatus FFT $D_e$ results versus $F_{ave}$ using different length pellets.
Old Apparatus $V_{\text{loop}} = 0.50 \times 10^{-6} \text{ m}^3$

$F_{\text{ave}} = 3.0 \times 10^{-6} \text{ m}^3/\text{sec}$

Figure 17. Old Apparatus experimental response curves for different length pellets
Figure 18. FFT $D_e$ results versus $F_{ave}$ for New A and Old Apparatus
3. New B

It was conjectured that $V_L$ being roughly $2 \times 10^{-6}$ m$^3$ might be responsible for incomplete mixing in the lower chamber of the cell. Relatively large residence times were thought to indicated poor mixing and the hold-up of tracer gas in dead spots in the bottom chamber could cause spreading of the experimental response curves which would explain the dependence of $D_e$ on $L$.

After the lower chamber was filled with paraffin, as described previously, experiments were performed with Pellet #514. The $D_e$ results obtained when using the New B apparatus were only slightly different than the results obtained when using the New A apparatus. To try to see the effect of $V_L$ on the value of $D_e$ calculated, the old value for $V_L$ of $2.004 \times 10^{-6}$ m$^3$, instead of $0.547 \times 10^{-6}$ m$^3$, was put into the FFT analysis program. The change in the value of $D_e$ calculated using this change in $V_L$ was quite large for $F_{ave} = 1.0 \times 10^{-6}$ m$^3$/s, but decreased rapidly to only 3% for $F_{ave} = 10.0 \times 10^{-6}$ m$^3$/sec.

4. New C

Before the flow that lead to the TCD was split, the effect of He concentration on the response of the TCD was measured. A N$_2$ flow was established through the sample side of the TCD and $0.50 \times 10^{-6}$ m$^3$ mixtures of He/N$_2$ were injected into this carrier stream using the six-port GC valve. Flows of the N$_2$ stream were $0.95 \times 10^{-6}$ and $4.5 \times 10^{-6}$ m$^3$/sec and calibrated rotameters were used to mix sample gas concentrations ranging from 10 to 100% He. All 512 of the data values collected were used when calculating the moments of the data. Five
runs at each condition were analyzed and their results averaged.

For both N₂ carrier flow rates, the values of μ₁ calculated for all the sample gas concentrations were within ± 0.09 seconds from the mean. For the lower carrier flow rate, the average μ₁ values were scattered about the mean, while the μ₁ values for the higher N₂ carrier rate showed a trend of slightly decreasing μ₁ value with decreasing He concentration. It was this dependence of μ₁ on x₃He in the sample stream of the TCD, at this higher flow rate, that led to the decision to reduce the flow rate of the sample stream through the TCD. To reduce the flow rate through the TCD and still obtain relatively high flow rates through the bottom of the cell, the flow was split as previously described.

The effect of splitting the flow to the TCD can be seen in Figure 19. The flow to the TCD was maintained at 1.0x10⁻⁶ m³/sec and the balance of the lower flow was passed through metering valve M9. A large portion of the apparent flow rate dependence of Dₑ was caused by the inability of the TCD to properly detect He in the sample stream.

To try to have the diffusional process dominate the measured response, pellets pressed at 37.2 kN (8370 lbf) were used in the remaining experiments. Longer pellets were also used and were pressed as composite pellets since pressed unlubricated pellets with more than 8x10⁻³ kg of powder developed density gradients. Pellets pressed at forces higher than 37.2 kN using the single-action die either expanded slightly out past the bottom of the ring after being pressed or cracked during the removal of the plunger from the ring. Because of these
Figure 19. FFT $D_e$ results versus $F_{ave}$ for New B and New C

Pellet #514

New A  $V_{Loop} = 0.61 \times 10^{-6} \, \text{m}^3 \times$

New C  $V_{Loop} = 1.90 \times 10^{-6} \, \text{m}^3 \diamond$
limitations, these were the highest compaction forces imposed upon the pellets.

To determine if He tracer gas concentration or sample loop size influenced the value of \( D_e \) calculated, experiments were performed with different concentrations of He in the injected samples and using different size sample loops. Figure 20 shows the effect of tracer gas concentration on the value of \( D_e \) calculated. For \( V_{\text{Loop}} = 5.21 \times 10^{-6} \, \text{m}^3 \), the values of \( D_e \) calculated at \( F_{\text{ave}} = 10 \times 10^{-6} \, \text{m}^3/\text{sec} \) differed by 9% between \( x_{\text{He}} = 9.86 \) and 100%. The effect of sample loop size on the value of \( D_e \) calculated is shown in Figure 21. Again, the values of \( D_e \) calculated at \( F_{\text{ave}} = 10 \times 10^{-6} \, \text{m}^3/\text{sec} \) differ by approximately 9% when using \( V_{\text{Loop}} = 0.15 \times 10^{-6} \) and \( 5.21 \times 10^{-6} \, \text{m}^3 \).

The variation of \( D_e \) with \( L \) for the 37.2 kN pressed pellets is shown in Figure 22. Pellet #520 was the largest pellet that could be used since the detection limit of the equipment was reached. Also shown in Figure 22 are the values of \( D_e \) calculated by using the difference in moments for Pellets #520 and #516. The \( D_e \) values obtained from the difference in moments, assuming infinite flow rates, are also shown in Figure 22.

Up to this point, all the results presented have been for the bottom feed of the cell entering the bottom of the cell. Experiments were performed on Pellet #522 to see the effect of moving the feed of the lower stream to the side of the diffusion cell and the manometer lead to the bottom of the cell. More experiments were performed, with the height of the cone above the face of the pellet, \( LY \), increased.
Figure 20. FFT $D_e$ results versus $F_{ave}$ for Pellet #516 using different tracer gas concentrations

**Pellet #516**

New A $V_{Loop} = 5.21 \times 10^{-6} \text{ m}^3$

- $X_{He} = 100. \%$
- $X_{He} = 52.5 \%$
- $X_{He} = 9.86 \%$
Figure 21. FFT $D_e$ results versus $F_{ave}$ for Pellet #516 using different size sample loops
Figure 22. FFT and difference in moment $D_e$ values versus $F_{ave}$ for pellets pressed at 37.2 kN
greatly. The results of these experiments, with \( V_{\text{cone}} = 0.901 \times 10^{-6} \text{ m}^3 \), along with the previously calculated \( D_e \) values obtained from the difference in moments for Pellets #520 and #516, are shown in Figure 23.

C. Tortuosity Calculations

The values of the product \( rD_e \), calculated using various procedures, are summarized in Table 6. The values of \( r_{\text{mode}} \), \( r_{\text{mean}} \), and \( r_{\text{cyl}} \) used in calculating \( rD_e = \epsilon_p D_T(r) \) were obtained from Table 4. The value of \( \epsilon_p \) was taken to be \( \epsilon_{p_m} \), except for Pellet #400, which used the value of \( \epsilon_{p_g} \). A plot of some of the values of \( rD_e \), from Table 6, versus \( \epsilon_p \), are shown in Figure 24. The straight lines shown in the figure are linear regression fits to the data. For \( \gamma_A = 0 \), lines below the line for \( \epsilon_p D_e \) represents the Knudsen contributions to \( D_T(r) \).

For a pellet pressed at 37.23 kN, high and low estimates of \( r \) can be made. In making these estimates, the low value of \( D_e \) used will be taken as the value obtained for Pellet #520 at \( F_{\text{ave}} = 10.3 \times 10^{-6} \text{ m}^3/\text{sec} \): the largest value of \( D_e \) obtained using the FFT procedure. The high estimate is taken as the \( D_e \) value obtained using the difference in moments procedure using the moment results from Pellet #520 and Pellet #516. Using \( rD_e = 1.34 \times 10^{-5} \text{ m}^2/\text{sec} \), from Table 6, and \( D_e = 4.72 \times 10^{-6} \text{ m}^2/\text{sec} \), the high estimate of \( r \) is 2.84. Using \( rD_e = 0.81 \times 10^{-5} \text{ m}^2/\text{sec} \), from Table 6, and \( D_e = 5.18 \times 10^{-6} \text{ m}^2/\text{sec} \), the low estimate of \( r \) is 1.56.
Figure 23. Affect of $F_L$ feed position and $L_{VU}$ on $D_e$ values.
Table 6. $\tau D_e$ calculated using different procedures

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</tr>
<tr>
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Figure 24. $\tau_D$ versus pellet porosity
VI. DISCUSSION

A. ZnS Powder and Pellet Characterization

Taking into account that the ZnS particles were not spherical, nor of a single particle size, excellent agreement among the different procedures used to calculate average particle diameters was found. The 0.16 μm value of \( \overline{D}_{BET} \) agrees quite well with the values of \( \overline{D}_{SEM} \) and \( \overline{D}_{TEM} \) when median values of \( \overline{D}_{SEM} = 0.16 \mu m \) and \( \overline{D}_{TEM} = 0.14 \mu m \), were chosen. To obtain a value of \( \overline{D}_{SED} \) equal to 0.16 μm, the selection of a value other than 50 cumulative wt% would have been necessary.

The results of the BET and mercury porosimetry experiments support the contention that micropores are absent from the powders and pellets and that the pore structure is composed of mesopores and macropores. Much larger values of \( C_{BET} \) and \( S_g \) would have been obtained if micropores were present and the high pressure mercury porosimetry intrusion experiments would have shown mercury intrusion in the micropore region. With the absence of a microporous structure in the pellets, a diffusional loss term to micropores in the diffusion model is not necessary.

The \( \rho_{ZnS} \) determinations indicate that using the literature value given by Perry and Chilton (1973), in calculating \( \varepsilon_{pg} \), was a reasonable choice. The agreement between the \( \varepsilon_{pg} \) and \( \varepsilon_{pm} \) values in Table 4 is quite good. Except for Pellet #402, the difference between the two values is roughly 3 to 4%.

Pellets pressed with more than 8.00x10^{-3} kg of powder had to be pressed as composite pellets to avoid density gradients. Pellet #514,
pressed as an unlubricated pellet with $16.00 \times 10^{-3}$ kg of powder, developed a significant density gradient, as indicated by the values of $\epsilon_{pg}$ found in Table 5. A powder sample pressed as a lubricated pellet had the undesirable characteristic that when pressed out of its ring, the pellet developed fracture planes parallel to its face and the pellet would break into thin wafers instead of retaining its pressed form. The shearing was thought to be caused by the lubricant being trapped with the powder near the edge of the ring and thus preventing the powder from compacting firmly. The lubricant might have also allowed the pellet to expand after compaction, a fact that was not observed with the pellets pressed without lubricant. To avoid contamination of the ZnS powder, no other lubricants were tried. The composite pellets were successfully pressed without density gradients shown by the $\epsilon_{pg}$ values of Pellets #502, #516, #519, #520, and #522.

Pellets pressed isostatically had pore size distributions similar to the distributions of unlubricated pellets when $4.00 \times 10^{-3}$ kg of powder were used. Density gradient-free pellets of more than $8.00 \times 10^{-3}$ kg of powder pressed isostatically as a single pellet might have been obtained, but this was not tried since the bottom of the pellet would not then be flush with the bottom of the pellet holding ring and this could hinder mixing in the lower chamber.

As mentioned previously, pellets pressed above 37.23 kN, using the single-action die, developed cracks or expanded past the bottom of the ring. Even though hardened steel was used for the construction of the pellet holding rings, it is believed that during the pellet pressing,
the force exerted on the powder caused the ring to expand. Then, when the pressing force was removed, the ring resumed its previous shape and its contraction caused the expansion or cracking of the pellet.

B. Diffusion Results

Although it may be difficult to draw hard conclusions using the diffusion results obtained before the flow to the TCD was split, several observations on the performance of the FFT procedure were made. The most powerful discovery made was that the FFT procedure effectively iterates on the characteristic diffusion time, $\tau_0 = L^2 \epsilon_p / D_e$. When the parameters in the diffusion model, $F_U$, $F_L$, $V_U$, $V_L$, $L$, $\epsilon_p$, and $A$, were varied by ±10%, the parameters that caused the largest change in the iterated value of $D_e$ were $L$ and $\epsilon_p$. Examination of the LT solution, $\overline{C_L}$, shows that $L$ only appears in the exponential terms of the solution. It was found that when $L$ and/or $\epsilon_p$ were varied, the characteristic diffusion time remained essentially constant.

With the Old Apparatus, the large dependence of $D_e$ on $L$ becomes apparent. As shown in Figure 17, the different length pellets produced similar response curves. With the response curves so similar, changing the value of $L$ in the FFT procedure changes the iterated $D_e$ value to keep the group $\tau_0$ constant. The $D_e$ values that would have been obtained if the runs of Pellet #512 were analyzed using different $L$ values and the $D_e$ values obtained experimentally for the same $L$ values, are shown in Table 7 for $F_{ave} = 3.0 \times 10^{-6}$ m$^3$/sec. Column 4 is the ratio of the experimentally determined $D_e$ values. Column 5 is the ratio of the $D_e$ values obtained using $\tau_0$ for Pellet #512 with different $L$.
Table 7. Comparison of old apparatus experimental $D_e$ values to $D_e$ values calculated for Pellet #512 using different L values

<table>
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<th>Pellet</th>
<th>$L$ (mm)</th>
<th>$D_e \times 10^6$ (m$^2$/sec)</th>
<th>$D_e$ / $D_e$ (#512)</th>
<th>$D_e$ (#512) / $D_e$ (#512)$_{L=1.74}$ mm</th>
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<tbody>
<tr>
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<td>0.113</td>
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<td>15.8</td>
</tr>
</tbody>
</table>

values. The tabulated experimental $D_e$ values are relatively close to the $D_e$ values obtained using different L values in analyzing the response curves of Pellet #512. This shows how little the pellet length used in the Old Apparatus effected the response curves obtained.

When the dead volumes were reduced in the conversion of the Old Apparatus to New A, the spread of the response curves, characterized by $\mu^2$, was reduced slightly. For experiments performed at fixed experimental conditions, a reduction in the spread of a response curve corresponds to an increase in the value of $D_e$ obtained from the FFT procedure. When trying to account for the dispersion of the tracer travelling to and from the diffusion cell with a bypass experiment, the values of $D_e$ obtained did not increase enough to explain the length dependence of the diffusivities. Although it may be argued that the bypass flow did not travel through the same fittings as the flow of the gas during a dynamic experiment, the difference in the flow pattern is not believed to be large enough to cause significant changes in the
shape of the bypass response curves or the values of $D_e$ calculated when using an experimental bypass response curve as the forcing function.

When the lower chamber volume was reduced, in the conversion of New A to New B, the $D_e$ values obtained did not change significantly for flows of $F_{ave}$ above $3.0 \times 10^{-6}$ m$^3$/sec. At $F_{ave} = 1.0 \times 10^{-6}$ m$^3$/sec, the $D_e$ values obtained from New B were larger than the corresponding $D_e$ values obtained from data from New A. However, above $F_{ave} = 3.0 \times 10^{-6}$ m$^3$/sec, the difference in the average $D_e$ values only ranged from 1 to 5%.

As shown in Figure 19, the effect of splitting the flow to the TCD on the values of $D_e$ calculated, was dramatic. Figure 25 shows two scaled experimental response curves for Pellet #514 when using New B and New C at the same operating conditions: the response curve for New B was shifted 13 data values away from the origin to compensate for the additional lag-time required for the response curve for New C to travel to the TCD. As shown in the figure, the response curve for New B is narrower than the response curve for New C. A plot of the experimental response curve for Run #1007, for Pellet #514 in New A at $10. \times 10^{-6}$ m$^3$/sec, gives a plot similar to that of Run #1061 and was omitted from the figure.

This narrowing of the response curve was interpreted as the inability of the TCD to detect all the He in the sample stream at high flow rates. The narrower curve gave a higher $D_e$ value than the curve obtained from the split flow configuration. As $F_L$ increased when using apparatus without the split flow, the narrowing of the response curve became greater. This effect explains part, but not all, of the
Pellet #514

\[ V_{\text{Loop}} = 1.90 \times 10^{-6} \text{ m}^3 \]

\[ F_{\text{ave}} = 10.0 \times 10^{-6} \text{ m}^3/\text{sec} \]

Figure 25. Effect of TCD split flow on experimental response curves using New C
dependence of $D_e$ on flow rate. As shown in Figure 13 for the runs performed with $F_U$ increasing for fixed $F_L$, there is a flow rate dependence of $D_e$ which is not caused by inadequate detection of the TCD. As seen in Figure 19, there is still a dependence of $D_e$ on flow rate.

As was shown in Figures 20 and 21, the effect of sample loop size and $\chi_{He}$ on $D_e$ was approximately 9% at $F_{ave} = 10.0 \times 10^{-6} \ m^3/sec$. Similar results were found for experiments performed on Pellets #515, #517, #518, and #519. The relatively smaller value of $D_e$ at $F_{ave} = 1.0 \times 10^{-6} \ m^3/sec$ for a $5.21 \times 10^{-6} \ m^3$ tracer sample is a result of violating assumptions used in deriving the diffusion model. With a relatively large volume of tracer gas being introduced into the upper chamber at a low flow, the impulse forcing function assumption is violated. Moreover, a large sample size allows the concentration of tracer in the pellet to rise and the assumption of a composition independence of $D_e$, is violated. Although some composition dependence of $D_e$ exists at higher flow rates, the use of dilute composition tracer gas reduced the detection sensitivity. For the longest pellet used in this study, Pellet #520, pulses of pure He in a $5.21 \times 10^{-6} \ m^3$ sample loop were necessary to obtain a detectable signal at high $F_{ave}$ values.

To determine if filling Cone A with window glazing and having the tracer introduced into $V_U$ through the $1.59 \ mm (1/16")$ tubing affected the mixing in the upper chamber, experiments were performed at $F_{ave} = 5.0 \times 10^{-6} \ m^3/sec$ on Pellet #522, at constant $V_U$ values with different $V_{cone}$ values. Five runs were performed with the cone filled with
glazing and \( L_{\text{VU}} \) was adjusted to 2.28 mm to give \( V_{\text{U}} = 1.16 \times 10^{-6} \text{ m}^3 \).

Five runs were also performed with the glazing removed from Cone A and \( L_{\text{VU}} \) adjusted to 0.53 mm to give \( V_{\text{U}} = 1.17 \times 10^{-6} \text{ m}^3 \). The difference between the average \( D_e \) values obtained from these runs was 0.38\% and it appears that the gas dispersion ability of Cone A has little effect on the \( D_e \) values calculated. Unless stated otherwise, experiments performed on Pellet \#522 were done with the glazing removed from Cone A.

To determine if pressure gradients across the length of the pellet could contribute to mass transfer through the pellet, experiments were performed at \( F_{\text{ave}} = 5.0 \times 10^{-6} \text{ m}^3/\text{sec} \) on Pellet \#522 with a pressure differential across the pellet which was measured with the water filled manometer. An estimation of the stagnation pressure of the top flow stream at \( 10. \times 10^{-6} \text{ m}^3/\text{sec} \) impinging on the pellet was 483 Pa (0.07 psig). Experimentally, a much larger pressure gradient was applied to the pellet. Pressure differences of approximately 3.43 kPa (350 mm \( H_2O \)) were applied across the pellet by increasing or decreasing the pressure in the upper chamber. Differences in the \( D_e \) values obtained, compared to the pressure-gradient-free results, were less than 0.5\% for both pressure differentials imposed.

The dependence of \( D_e \) on feed position of the flow into the bottom of the cell and on \( L_{\text{VU}} \), the cone height, was shown in Figure 23. The flow rate dependence of \( D_e \) was virtually eliminated when the feed location of \( F_l \) was switched from the bottom to the side of the cell. Increases in \( D_e \) of over 10\% were found at \( F_{\text{ave}} = 10. \times 10^{-6} \text{ m}^3/\text{sec} \) when
using different feed configurations. Although it was unfortunate that so many of the dynamic experiments were performed with the $F_L$ feed to the bottom of the cell, experiments performed with New B, with the bottom feed switched to the side of the cell, did not give significantly different results and the $F_L$ feed was returned to the bottom of the cell so additional runs could be compared to previous results.

The variation of $D_e$ with $L_{UU}$ was also shown in Figure 23. For $L_{UU} = 0.53$ mm, $V_U$ was $1.17 \times 10^{-6}$ m$^3$, while $L_{UU} = 8.26$ mm corresponded to $V_U = 5.09 \times 10^{-6}$ m$^3$: these upper chamber volumes included the volume of Cone A since the glazing was removed from the cone for these runs. Although the cone height of 8.26 mm was an extreme case, and no other experiments were performed with cone heights near this value, these results demonstrate that the value of $L_{UU}$ can affect the calculated $D_e$ values by 6% without showing a flow rate dependence.

In the CMDWKDC model, the assumption is made that the region between the cone and the pellet is a well-mixed chamber in contact with a stagnant layer of gas which is in contact with the top of the pellet. When applying the CMDWKDC model, with $\epsilon_1 = 1.00$ and $D_1 = 0.701 \times 10^{-4}$ m$^2$/sec, to the runs performed on Pellet #522 with $L_{UU} = 8.26$ mm, the values of $D_e$ obtained with $\text{FRACTM} = 0$ were within 6% of those obtained for Pellet #520 with $\text{FRACTM} = 1$; however, when applying the same procedure to the runs performed on Pellet #522 with $L_{UU} = 0.53$ mm, the $D_e$ values obtained were scarcely different than the results obtained with $\text{FRACTM} = 1$. These results indicate that the $L$ dependence of $D_e$
cannot be accounted for solely by running experiments with slightly different values of $L_{VV}$. For the results shown in Figure 22, Pellets #520, #519, and #516 had $L_{VV}$ values of 0.42, 0.60, and 0.82 mm, respectively, and these slight differences cannot explain the $L$ dependence of $D_e$.

The dependence of $D_e$ on $L$, for pellets pressed at 37.2 kN, was shown in Figure 22 and the $D_e$ values calculated from the difference in first moments were also shown in the same figure. Although the $D_e$ dependence on $L$ is decreasing as pellet length increases, it has persisted to the point where longer pellets could not be analyzed. It had been speculated that the values of $D_e$ calculated from the difference in moments may be the asymptotic values of $D_e$ since the only differences in the measured response curves are due to the diffusion of gas through an additional length of pellet and non-idealities of the system would be subtracted from one another and their effects eliminated. $D_e$ values calculated using the difference in moments procedure for Pellets #520 and #516, and Pellets #520 and #519, differ by less than 3%.

The possibility that the $L$ dependence of $D_e$ was caused by diffusion in the radial direction was investigated. As can be inferred from the data in Table 5, the pellet length-to-radius ratios, $LR$, are relatively small. If radial diffusion was present in the pellet, the larger the value of $LR$, the less effect this radial diffusion would have on the calculated value of $D_e$.

Analytically, a simplified diffusion model was solved to
investigate qualitatively the effect of having a non-uniform concentration imposed at the center of the pellet at time zero. The equations used for the simplified model were

\[
\frac{\partial C_R}{\partial \tau} = \frac{\partial^2 C_R}{\partial \theta^2} + \left( \frac{LR}{\Theta} \right)^2 \left( \frac{1}{\Theta_R} \frac{\partial C_R}{\partial \theta} + \frac{\partial^2 C_R}{\partial \theta^2} \right) \quad 0 < \theta < 1
\]

\[
\frac{\partial C_R}{\partial \theta} \bigg|_{\theta=0} = \frac{\partial C_R}{\partial \theta} \bigg|_{\theta=1} = 0
\]

\[
\frac{\partial C_R}{\partial \theta} \bigg|_{\theta=0} = 0
\]

\[
-D \frac{\partial C_R}{\partial \theta} \bigg|_{\theta=1} = k_f C_R \bigg|_{\theta=1}
\]

\[
C_R = \frac{\pi(\Theta = 1)^2}{\pi(\Theta_R)^2} C_0 \delta(\Theta_z)
\]

where \( C_R \) = concentration in pellet,

\( \Theta = \) dimensionless time, \( t/\tau_D \),

\( \Theta_z = \) dimensionless longitudinal direction,

\( \Theta_R = \) dimensionless radial direction, and

\( \Theta_r = \) dimensionless radius of sample pulse.

The dimensionless radius of the sample pulse, \( \Theta_r \), is the radius for the area in which the initial gas pulse will be introduced and can vary between 0 and 1. For \( \Theta_r = 1 \), this would correspond to a uniform concentration across the top of the pellet. For \( \Theta_r = 0 \), this corresponds to a point source concentrated at the center of the pellet.
The solution for the previous set of equations is

$$C_R = \sum_{m=1}^{\infty} A_m \cos(\gamma_m \theta_z) e^{-\gamma_m \theta \tau}$$

$$+ \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} A_{nm} J_0(\beta_n \theta_R/LR) \cos(\gamma_m \theta_z) e^{-(\beta_n^2 + \gamma_m^2) \theta \tau}$$

$$\text{where } A_m = \frac{C_0}{[1 + \frac{k_f/D_e}{\gamma_m^2 + \left(\frac{k_f}{D_e}\right)^2}]}$$

$$A_{nm} = \frac{C_0}{J_0^2(\beta_n/LR)} \left[1 + \frac{k_f/D_e}{\gamma_m^2 + \left(\frac{k_f}{D_e}\right)^2}\right]$$

$$A_{nm} = \frac{4C_0 J_1(\beta_n \theta_R/LR)}{(\beta_n \alpha/f) J_0^2(\beta_n/LR)} \left[1 + \frac{k_f/D_e}{\gamma_m^2 + \left(\frac{k_f}{D_e}\right)^2}\right]$$

and where the eigenvalues for $\beta_n$ and $\gamma_m$ are the non-zero roots of

$$J_1(\beta_n/LR), \text{ and } (\gamma_m)\tan(\gamma_m) = k_f/D_e.$$  \hspace{1cm} (134)

The first term in the solution of $C_R$ is the solution for radial independent diffusion, $\beta_n = 0$, and the second term is the radial diffusion contribution to the solution. For $\theta_R$ going to zero and $LR > 2$, the radial concentration profiles at $\theta_z = 1$ were barely affected by the point source initial condition. For $LR = 1$, significant
differences in the radial profiles were seen for \( \frac{k_f}{D_e} = 1 \) and 10, but the profiles flattened-out faster for \( \frac{k_f}{D_e} = 10 \).

Limited utility of this simplified model became apparent when trying to compute average concentrations. Average concentrations were computed using

\[
\overline{C_R} = \frac{2\pi}{\int_0^1 \int_0^{\pi} \frac{C_\theta d\theta d\phi}{R^2}}
\]

When the above integrations were performed, the radial dependence of the diffusional process was eliminated: the average concentration at the bottom of the pellet was the same as for the radially-independent diffusion problem.

To experimentally investigate the effect of the inlet location for \( F_U \) on the calculated value of \( D_e \), a series of experiments were performed with Cone B. Using Pellet #522, with the \( F_U \) feed from the side of the cell and \( L_{UU} = 0.75 \) mm, experiments were performed with \( F_{ave} = 5.0 \times 10^{-6} \) m\(^3\)/sec and \( 10.0 \times 10^{-6} \) m\(^3\)/sec, for several variations for the feed of \( F_U \) into the upper chamber. In the first series, the four gas inlet holes near the perimeter of the cone were filled with glazing to see if the same diffusion results would be obtained using Cone B as when using Cone A. The second configuration was to have the \( F_U \) flow enter the upper chamber through one of the holes near the perimeter of the cone with the other four gas inlet holes plugged. The final configuration was to plug the center hole in Cone B and allow the tracer to enter the chamber through the four holes near the perimeter.
of the cone.

At $F_{ave} = 10 \times 10^{-6} \text{ m}^3/\text{sec}$, the results obtained using all three configurations of Cone B gave the same results as when using Cone A at the same operating conditions. At $F_{ave} = 5.0 \times 10^{-6} \text{ m}^3/\text{sec}$, $D_e$ obtained when only the center hole of Cone B was used for gas flow was approximately 5% smaller than the $D_e$ results using Cone A at the same conditions; the other two configurations gave $D_e$ that were approximately 4% smaller. These results show that although Cone B was thought to be a superior design for gas dispersion, a larger flow rate dependence was observed than when using Cone A.

To see what effect adjustment of the lag-time parameter, $P_2$, had on the value of $D_e$ obtained by using the FFT procedure, results for two different length pellets were compared when using $V_{loop} = 5.21 \times 10^{-6} \text{ m}^3$, $x_{He} = 100\%$, and $F_{ave} = 5.0 \times 10^{-6} \text{ m}^3/\text{sec}$. For Pellet #516, Run #1325, and for Pellet #520, Run #1720, the iterated values of $D_e$ and $P_2$ were $2.69 \times 10^{-6} \text{ m}^2/\text{sec}$ and 1.79 sec, and $4.48 \times 10^{-6} \text{ m}^2/\text{sec}$ and 2.52 sec, respectively. When fixing the value of $P_2$ equal to 2.55 sec, the average $P_2$ value for the runs performed on Pellet #520, for Run #1325, the iterated value of $D_e$ was $3.39 \times 10^{-6} \text{ m}^2/\text{sec}$. Similarly, when the value of $P_2$ was fixed to 1.80 sec for Run #1720, the iterated value of $D_e$ was $4.21 \times 10^{-6} \text{ m}^2/\text{sec}$. As with the other pellets, as $L$ increased, $P_2$ increased. If the value of $P_2$ was fixed in the iteration procedure, the results obtained for shorter pellets would be affected drastically by errors in the estimated values of $t_{lagd}$. On the other hand, for long pellets like Pellet #520, the $D_e$ value is reduced only by 6% when
using a fixed lag-time value which is 0.72 sec shorter than the FFT iterated value.

It was suggested that the inclusion of the response time of the TCD into the diffusion model could possibly explain the length dependence of the $D_e$ values and the effect of this response time on $D_e$ calculations was investigated. A step change in gas concentration to the TCD from 100% $N_2$ to a mixture of 9.86% He in $N_2$ was made by modifying tubing connections to and from the six-port GC valve, removing the diffusion cell and the cone, and passing all the gas flow through the sample side of the TCD at approximately $0.94 \times 10^{-6}$ m$^3$/sec.

The response of the system was assumed to be first-order with a time-lag. The time constant of the system was determined by calculating the time after the start of the response that corresponded to $(1-e^{-1})$ times the height of the step-change response; the value obtained was 1.35 sec and comparison of the first-order model to the data was good. The inclusion of the transfer function of the TCD into the model was performed in the FFUNCT subroutine of the program found in Appendix C.

Blank runs, dynamic experiments performed on the diffusion cell when Pellet #521 was used in the cell, had been performed previously at $F_{ave} = 5.1 \times 10^{-6}$ m$^3$/sec with $V_{loop} = 5.21 \times 10^{-6}$ m$^3$ and $x_{He} = 100%$; they were used to determine the additional effect dispersion of the flow through the system had on the $D_e$ values obtained from the FFT procedure. Run #1746 was chosen for use from the five blank runs performed since its moments were closest to the average value of the
five blank runs performed.

For Pellet #516, Run #1325, which was obtained for $F_{ave} = 5.0 \times 10^{-6}$ m$^3$/sec, $V_{loop} = 5.21 \times 10^{-6}$ m$^3$, and $X_{He} = 100\%$, was used for analysis. Previously, $D_e$ was calculated to be $2.69 \times 10^{-6}$ m$^2$/sec when using an impulse forcing function in the model. When using Run #1746 as the forcing function, $D_e$ obtained was $3.39 \times 10^{-6}$ m$^2$/sec. Using an impulse forcing function and including the first-order response of the TCD in the model gave $D_e = 3.95 \times 10^{-6}$ m$^2$/sec while the blank run with the TCD transfer function included gave $D_e = 5.30 \times 10^{-6}$ m$^2$/sec. This last value is 4.3% higher than the average $D_e$ obtained from difference in moment calculations. Similar results for Pellet #519 gave $D_e$ values of $3.75 \times 10^{-6}$, $4.17 \times 10^{-6}$, $4.47 \times 10^{-6}$, and $4.96 \times 10^{-6}$ m$^2$/sec, respectively, and the last $D_e$ value is 2.4% lower than the corresponding difference in moments value. $D_e$ values obtained by modifying the diffusion model to include the response of the TCD and the dispersion of the pulse agree quite well with the difference in moments values. The ability to calculate similar $D_e$ values using two different procedures, the FFT procedure and the difference in moments procedure, is strong support for either calculation procedure and the length dependence of diffusivity values can be eliminated. Even though the use of blank runs for representing dispersion of the flow through the apparatus is an approximation, incorporation of dispersion effects into the diffusion model is necessary to eliminate the length dependence of $D_e$.

When examining the values of $\tau D_e$ presented in Table 6, the values obtained by assuming a cylindrical pore geometry agree the best with
the results obtained by integrating $D_T(r)$ over all pore sizes. The agreement between $\epsilon_p D_T(r)$ when evaluated at $r_{mode}$ is not quite as good as when assuming a cylindrical pore geometry with the differences between the $r_{mode}$ results and the integrated results varying from 7 to 8% for $\gamma_A = 0$, and 4 to 30% for $\gamma_A = 1$. The value of $\tau D_e$ obtained when evaluating $D_T(r)$ at the volume-averaged pore radii gave the poorest agreement to the results obtained from integrating over all pore sizes. For $\gamma_A = 0$, differences ranged from 17 to 53%, and for $\gamma_A = 1$, the differences ranged from 16 to 66%.

The debate over which of these procedures is the preferred procedure is still open. Agreement between computing the product $\tau D_e$ two different ways does not necessarily make these two procedures better than the other methods: just more consistent with one another. The results of the integration procedures differ from 23 to 90% when $\gamma_A$ varies between 0 and 1. The difference between the $D_e$ values obtained when analyzing experiments performed with He tracer concentrations of 9.86 and 100% being roughly 10% or less supports the use of low values of $\gamma_A$ in $D_T(r)$ for any of the calculation procedures. Even though the extreme estimates of $\tau$ differ by almost 50%, experimental values ranging between 1.56 and 2.84 are quite reasonable.
VII. CONCLUSIONS

The FFT procedure described is the preferred method for calculating $D_e$ values when compared to calculations performed using moments of the response curves. The FFT $D_e$ values were more consistent with one another than the values calculated using moments: the FFT values were less sensitive to noise and drift in the response curves and to the procedures used to calculate the baseline and truncation point of the data sets: iteration on the value of $P_2$ compensated for errors in lag-time estimates.

The pressing of pellets as composite, unlubricated pellets eliminated density gradients in the pellets. The powder characterizations performed showed that the pellets were characterized by pores in the mesopore and macropore pore size ranges. In the absence of micropores and adsorption, the model for diffusion through the pellet could be described as shown in Equation (63) with a composition independent $D_e$ value being a reasonable assumption. However, at the temperature and pressure at which the diffusion experiments were performed, diffusion occurred in the transition region where both Knudsen and ordinary diffusion were present.

The way the upper and lower gas streams were entered into the diffusion cell could significantly affect the $D_e$ values calculated. Changing the lower gas flow from the bottom of the cell to the side of the cell had the effect of reducing the flow rate dependence of $D_e$ and larger values of $D_e$ were obtained. The height of the cone above the top of the pellet could also effect the $D_e$ values obtained, but the
differences could not be accounted for using the CMDWKDC model that was developed. The different $D_e$ values obtained using the same cone at different heights above the pellet showed that flow rate independence of $D_e$ is not sufficient criteria to justify all the assumptions made in deriving the diffusion equations for the DWKDC. The use of different cone designs can affect the $D_e$ values obtained and one can not predict a priori whether one cone design is better than another.

The splitting of the bottom flow stream to the TCD greatly reduced the observed flow rate dependence of $D_e$. The splitting of the flow was interpreted as allowing the TCD an adequate response time to detect the He in the carrier stream. The disadvantage of the flow splitting is that the detection limit of the system is greatly reduced at high flows.

The use of different He gas concentrations in the injected samples and different sample loop sizes gave differences among $D_e$ values that were less than 10% when an impulse forcing function was used in the model for moderate to high flow rates. Pressure differentials of approximately 3.4 kPa across a 19.6 mm pellet did not affect the value of $D_e$ calculated.

The design of the experimental apparatus affected the values of $D_e$ calculated. Apparatus dead volumes increased the spread of the response curves and gave lower $D_e$ values. Bypass experiments that completely bypassed the cell could not adequately compensate for the spreading of the response curves obtained. When relatively short pellets were used that did not contribute significantly to the spread
of the response curves, the length dependence of \( D_e \) could be partially explained in terms of similarly shaped response curves having values of the characteristic diffusion time, \( \tau_0 \), nearly the same.

When relatively longer pellets were analyzed, \( D_e \) increased with pellet length until the detection limits of the system were reached. The largest \( D_e \) values were calculated using the difference in first absolute moments for two pellets and values were within 3% of one another when calculated independently by using moment values from three pellets. The \( D_e \) values obtained for the longest pellet used and analyzed using the FFT procedure were within 10% of the difference in moment values and may have been closer to these values if the flow to the bottom of the diffusion cell had been from the side instead of from the bottom of the diffusion cell for these runs.

The simplified model proposed to investigate the influence of radial diffusion in the pellet failed. Although the model predicted that radial concentration profiles could be developed, the influence of the radial profiles on the value of \( D_e \) calculated could not be determined since the calculation of average concentrations eliminated the radial portion of the solution. Experiments performed to try and determine the effect of introducing the top feed at the center and near the edge of the pellet did not contribute any information to support or negate the notion of radially dependent diffusion in the pellet.

Consistent FFT \( D_e \) values could be calculated for different length pellets when the transfer function for the TCD and the dispersion of gas flow through the apparatus were included in the diffusion model.
Although the blank runs performed were approximations of the actual dispersion, the diffusivities calculated using these estimates were within 7% of one another when the results for two pellets of different lengths were analyzed.

Diffusivities calculated using this modified diffusion model were within roughly 4% of the values calculated using the difference in moments procedure. The ability to calculate similar diffusivity values using the two different procedures is strong support for using either calculation procedure since either procedure eliminates the length dependence of the diffusivity.

Values of $\tau_0e$ calculated by evaluating the total diffusivity at different radii, and by summing up contributions over all pore radii, did not differ enough from one another to make any one of the procedures the preferred procedure for use in tortuosity calculations. Using different values to calculate the tortuosity factor, $\tau$, gave reasonable values for both the low and high estimates of $\tau$: $\tau$ is between 1.56 and 2.84.
VIII. RECOMMENDATIONS

Better estimates of the dispersion of the flow through the apparatus need to be made to check the results obtained in this work. The use of a faster responding, more stable, detector may reduce the magnitude of dispersion in the detector, and thus in the measured response, and also reduce the effect of the detector transfer function on diffusivity calculations. A higher sensitivity detector would also allow relatively long pellets to be analyzed with tracer gas concentrations of less than 100% tracer. Other apparatus modifications that could be made include using mass flow controllers instead of metering valves, better pressure gauges with larger pressure ranges, and a variable sampling rate A/D converter so that fewer data points need to be recorded.

Another problem is thought to be in the design of the upper chamber of the diffusion cell. This design affects the flow pattern over the pellet and modifications should be made. A design similar to the present cell could be built with smaller diameter pellet rings. Using sample cones of similar design to those used in this study with the smaller diameter rings, the effect of having to spread the pulse of tracer over a smaller area could be observed. Although the detection limits of the system will require that pellets of the same LR ratio be used, the volumes for mixing above and below the pellet will be reduced.

Another cell design that is strongly recommended is to design a new cell with the upper chamber similar in design to the lower chamber
as used in this study. With both chambers using this design, the pellet holding ring could be held between the top and bottom of the diffusion cell as shown by Wakao (1974) so that the upper mixing volume would be reduced. One disadvantage of this cell design would be that pellets would have to be pressed into the ring with both faces flush with the ends of the ring.
IX. REFERENCES


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XI. APPENDIX A: COMPOSITE MEDIA DYNAMIC WICKE-KALLENBACH
DIFFUSION CELL MODEL SOLUTION AND MOMENTS
After taking the Laplace transforms of Equations (61)-(68) and using Equation (33), the following matrix system is obtained:

\[
\begin{bmatrix}
    a_{11} & a_{12} & 0 & 0 \\
    \phi_1(x=L_1) & \theta_1(x=L_1) & -\phi_2(x=L_1) & -\theta_2(x=L_1) \\
    -D_1\phi_1'(x=L_1) & -D_2\theta_1(x=L_1) & D_2\phi_2'(x=L_1) & D_2\theta_2'(x=L_1) \\
    0 & 0 & a_{34} & a_{44}
\end{bmatrix}
\begin{bmatrix}
    A_{11} \\
    B_{11} \\
    A_{22} \\
    B_{22}
\end{bmatrix}
= \begin{bmatrix}
    \bar{F}(s) \\
    0 \\
    0 \\
    0
\end{bmatrix}
\]

where

\[
a_{11} = (1+s\tau_U)\phi_1(x=0) - \Pi_1\phi_1'(x=0) = -\Pi_1\psi_1',
\]

\[
a_{12} = (1+s\tau_U)\theta_1(x=0) - \Pi_1\theta_1'(x=0) = (1+s\tau_U),
\]

\[
a_{34} = (1+s\tau_L)\phi_2(x=L_2) + \Pi_2\phi_2'(x=L_2),
\]

\[
a_{44} = (1+s\tau_L)\theta_2(x=L_2) + \Pi_2\theta_2'(x=L_2),
\]

\[
\Pi_1 = AD_1/F_U,
\]

\[
\Pi_2 = AD_2/F_L,
\]

and ' indicates differentiation with respect to \(x\). Since we are only interested in the solution at \(x=L_2\), we only need to solve for \(A_{22}\) and \(B_{22}\). Using Cramer's rule,

\[
A_{22} = \frac{\bar{F}(s)[D_1\psi_1][(1+s\tau_L)\cosh(\beta_2) + \Pi_2\psi_2\sinh(\beta_2)]}{\Delta},
\]

\[
B_{22} = -\frac{\bar{F}(s)[D_1\psi_1][(1+s\tau_L)\sinh(\beta_2) + \Pi_2\psi_2\cosh(\beta_2)]}{\Delta},
\]

\[
\Delta = -[\Pi_1\psi_1][\cosh(\alpha_1)\Delta_1 + D_1\psi_1\sinh(\alpha_1)\Delta_2] - [1+s\tau_U][\sinh(\alpha_1)\Delta_1 + D_1\psi_1\cosh(\alpha_1)\Delta_2],
\]

\[
\Delta_1 = [D_2\psi_2][(1+s\tau_L)\cosh(\beta_2 - \alpha_2) + \Pi_2\psi_2\sinh(\beta_2 - \alpha_2)],
\]

\[
\Delta_2 = [(1+s\tau_L)\sinh(\beta_2 - \alpha_2) + \Pi_2\psi_2\cosh(\beta_2 - \alpha_2)],
\]

\[
a_i = \psi_iL_1, \text{ } i=1,2, \text{ and }
\]

\[
\beta_i = \psi_iL_2, \text{ } i=1,2.
\]
Using
\[ \overline{C}_L = \overline{C}_2(x=L_2) = A_{22} \phi_2(x=L_2) + B_{22} \theta_2(x=L_2), \]
we get
\[ \overline{C}_L = \overline{F}(s) R_2 \psi_2 \]
\[ \frac{\overline{C}_L}{\overline{F}(s) \Pi_2 \psi_2} = \frac{[\Pi_1 \psi_1]\Gamma \cosh(\alpha_1) ((1+\tau_L)\cosh(\beta_2-\alpha_2) + \Pi_2 \psi_2 \sinh(\beta_2-\alpha_2))}{+ \sinh(\alpha_1) ((1+\tau_L)\sinh(\beta_2-\alpha_2) + \Pi_2 \psi_2 \cosh(\beta_2-\alpha_2))}
+ [1+\tau_L] [\Gamma \sinh(\alpha_1) ((1+\tau_L)\cosh(\beta_2-\alpha_2) + \Pi_2 \psi_2 \sinh(\beta_2-\alpha_2))]
+ \cosh(\alpha_1) ((1+\tau_L)\sinh(\beta_2-\alpha_2) + \Pi_2 \psi_2 \cosh(\beta_2-\alpha_2))], \]
where \( \Gamma = \frac{D_2 \psi_2}{D_1 \psi_1} = \left[ \frac{D_2 \epsilon_2}{D_1 \epsilon_1} \right]^{1/2}. \)

Defining
\[ R_1 = \frac{\Pi_1 D_2}{D_1} = AD_2/F_U, \]
\[ R_2 = \frac{\Pi_2 }{AD_2/F_L}, \]
\[ Q_1 = \lambda_2 \tau_u, \]
\[ Q_2 = \lambda_2 \tau_L, \]
and using \( s = \psi_2^2 \lambda_2, \)
we get
\[ \overline{C}_L = \overline{F}(s) R_2 \psi_2 \]
\[ \frac{\overline{C}_L}{\overline{F}(s) R_2 \psi_2} = \frac{[(R_1 Q_2 + R_2 Q_1) \psi_2^3 + (R_1 + R_2) Q_1 \psi_2^2 + 1] \cosh(\alpha_1) \sinh(\beta_2-\alpha_2)}
+ \frac{[(R_1 Q_2 + R_2 Q_1) \psi_2^4 + (R_1 + R_2) Q_1 \psi_2^2 + 1] \sinh(\alpha_1) \cosh(\beta_2-\alpha_2)}
+ \frac{[(R_1 Q_2 + R_2 Q_1) \psi_2^4 + (R_1 + R_2) Q_1 \psi_2^2 + 1] \sinh(\alpha_1) \cosh(\beta_2-\alpha_2) \cosh(\beta_2-\alpha_2)]}{\cosh(\alpha_1) \cosh(\beta_2-\alpha_2)}.
\]

The relationships between the variables used here and the variables used by Burghardt and Smith (1979) are:
\[ R_1/L = K_U = K_1 \text{ (B.S.)}, \]
\[ R_2/L = K_L = K_2 \text{ (B.S.)}, \]
\[ \frac{Q_1}{L^2} = H_U = H_1 \text{ (B.S.)}, \]
\[ \frac{Q_2}{L^2} = H_L = H_2 \text{ (B.S.)}, \]
\[ \psi^2 L^2 = \psi \text{ (B.S.)}, \text{ and} \]
\[ S_2 - \alpha_2 = \psi \text{ (B.S.)}. \]

For the limiting case of \( L_1 = 0 \), \( \overline{C}_L \) reduces to an equivalent form of the solution given by Burghardt and Smith (Equation (3.5), 1979).

For the limit as \( L_1 \to L_2 \), the expression reduces to the proper solution for gaseous diffusion in media 1 from 0 to \( L_1 \). For \( D_1 = D_2 \), \( \varepsilon_1 = \varepsilon_2 \), \( \Gamma \) is equal to one and the solution reduces to the proper form for diffusion through a continuous media of length \( L_2 \).

By differentiation of \( \overline{C}_L \) with respect to \( s \), as shown in Equation (11), the theoretical moments can be generated. The moments \( m_{OLI} \) and \( \mu_{1LI} \) are

\[ m_{OLI} = \frac{MK_L}{[1+K_U+K_L+K_X/K_D]} \]
\[ \mu_{1LI} = \frac{[L^2 \varepsilon^2_2/(6D_2)][6K_UK_L(1+K_X/K_D)+3(K_U+K_L)(1+K_X/K_D)K^2_X+3K_X^3K_D(K_X+1)K_D]}{[1+K_U+K_L+K_X/K_D]}
\]

\[ + \frac{\tau_U(1+K_U+K_X/K_D) + \tau_L(1+K_U+K_X/K_D)}{[1+K_U+K_L+K_X/K_D]}. \]

\( m_{OLI} \) and \( \mu_{1LI} \) reduce to the expressions of Burghardt and Smith (1979) when \( L_1 = 0 \): \( K_X = 0 \).
XII. APPENDIX B: DIFFUSION CELL, RING, AND CONE DRAWINGS
Figure 26. Scale drawing of diffusion cell bottom
Figure 27. Scale drawing of diffusion cell bottom
Figure 28. Scale drawings of Cone A, Cone B, and a pellet ring
XIII. APPENDIX C: COMPUTER PROGRAM FOR CALCULATING EFFECTIVE DIFFUSIVITIES
THIS PROGRAM ANALYZES EXPERIMENTAL DYNAMIC WICKE-KALENBAH DATA.


THE PROGRAM CAN MINIMIZE ON 0, 1, 2, OR 3 PARAMETERS.

THE ITERATION PARAMETERS IN THE PROGRAM ARE: P1=1/SQRT(D) = PAR(1), TLAG (LAG-TIME) = PAR(2), AND TPULSE = PAR(3) (SQUARE WAVE PULSE TIME)

IF SF=0., 'SCALE' IS DEFINED AS SCALE=REAL(YEMF(1))/REAL(CMODEL(1)):

THE RATIO OF THE TRANSFORMED DATA TO THE MODEL'S ESTIMATE AT S=0.

THIS SCALING FORCES THE AREA OF THE TWO CURVES, THE EXPERIMENTAL AND THE MODEL'S, TO BE THE SAME VALUE.

INTEGER I,J,KMAX,FLAG,DIRECT,NRUN,LY(4),IR(4)
INTEGER ESTMD,ESTMT,ATNB,ATND,AMPB,AMPD,RESB,RESD,AMPBM,NSQRWV
INTEGER N,NB,ND2,N1,N2,NPAR,NPLT,NBASE,NBASEB,NBYPAS,NEVAL
INTEGER NSMTH,NSMTHB,NDATA,NTOTAL,NMAX,NSIG,OPT,ITAIL,MAX
INTEGER IMF,ICALL,OUTMOD,OUTMIN,OUTPRT,SPLIT
REAL YERT(1024),YEMT(1024),YMODEL(1024),XERT(1024),XEMT(1024)
REAL TIME(1024),PAR(3),NEWPAR(3),HESSN(6),GRADNT(3),WORK(9)
REAL MOMRAW(6),MOMMOD(6),MOMSFT(6),MOMPRA(6),MOMTHR(6),MOMXEM(6)
REAL PI,PN,KN,K1,K2,H1,TAU2,B,TUUTC
REAL D,DNEW,TLAGM,TLAGD,TLAGDN,TLAGB,TINJ,DT,DDATA
REAL D1,PAR1,FRACT,KLV,KE,KE,KD,KE
REAL PMAX,PMAXB,SSQR,SSQRW,SCALE,C1,C2,C3,T1,T2,T3,T4
REAL TFU,TFI,LCONE,LRING,DIA,VCON,VLOOP,TFLS,VFLTC,F,SFLTC
REAL VDU,VDL,VINJ,VCV,VSBU,VSBU,VSFLS
REAL FN,FL,VL,AREA,LPAR,M2,M3,M4,M5,M6,M7,PAR1,PAR2,TPULSE,SF
COMPLEX8 ZN1,EP,EC,CCOH,CSINH
COMPLEX8 ESOLN(1024),CC1(513),CC2(513),CC3(513)
COMPLEX8 S(513),S12(513),YEMF(1024),M1(513),FS(1024)
COMMON/INTERS/N,ND2,N1,N2,NPAR,IFORCE,NSQRWV,ICALL
COMMON/REELS/FU,FL,VU,VL,AREA,L,POR,LVUD,D1,PARI,PAR2,TPULSE,SF
COMMON/FORCF/XERT,XEMT,DT,TINJ,TAUTCD
COMMON/IMGS/S,S12,YEMF,M1,FS,CC1,CC2,CC3
EXTERNAL

C **************************************************
C SET EXPONENTIAL UNDERFLOW TO ZERO
C CALL TRAPS (0,0,20)
C READ INPUT DATA
C IF SPLIT .NE. 0, THE FLOW FROM THE BOTTOM OF THE CELL IS SPILT
C BETWEEN THE TCD AND ANOTHER STREAM.
C READ (10,214) NRUN
C READ (10,214) NDATA
DO 200 I=1,NDATA
   READ (10,218) YERT(I)
200   YEMT(I)=YERT(I)
C READ(11,214) NPLT
READ (11,215) ATND,AMPD,RESD
READ (11,221) TFU,TFL
READ (11,221) VCON,VL
READ (11,223) VDU,VDL,VLOOP
READ (11,221) DIA,LRING,LCONE
READ (11,221) L,POR
READ (12,214) NPAR,IFORCE,NSQRWV,TPULSE
READ (12,224) NSMTH,NSMTHB
READ (12,214) ESTMD,ESTMT,AMPBM
READ (5,215) KMAX,NSIG,LOPT
READ (5,221) TFU,TFL
READ (5,221) VCONE,VL
READ (5,223) DIA,LRING,LCONE
READ (5,223) L,POR
READ (5,224) NPAR,IFORCE,NSQRWV,TPULSE
READ (5,227) NSMTH,NSMTHB
READ (5,228) NTOTAL,NMAX,DTDATA
READ (5,215) ESTMD,ESTMT,AMPBM
READ (5,215) KMAX,NSIG,LOPT
READ (5,215) OUTMOD,OUTMIN,OUTPRT
READ (5,230) PMAX,NBASE
READ (5,230) PMAXB,NBASEB
READ (5,233) D
READ (5,233) TLAGD
READ (5,234) FRACTM
READ (5,233) D1
READ (5,234) POR1
READ (5,234) TAUTCD
IF (IFORCE.NE.2) GO TO 212
READ (12,214) NBYPAS
READ (12,214) NB
IF (NB.EQ.NDATA) GO TO 206
WRITE (6,203)
203 FORMAT (' N (BYPASS DATA) .NE. N (DYNAMIC DATA) ')' )
GO TO 999
206F, DO 209 I=1,NB
209 READ (12,218) XERT(I)
READ (5,215) ATNB,AMPB,RESB
READ (5,214) SPLIT
IF (SPLIT.NE.0) READ (11,221) TFLS,VDLTD
READ (5,214) NEVAL
FLAG=0
IF (NTOTAL.LE. NDATA) GO TO 239
WRITE(6,236) NTOTAL, NDATA
FLAG=99
236 FORMAT(' NTOTAL =',15,' -GT. NDATA =',I5)
IF (NTOTAL.EQ.64 .OR. NTOTAL.EQ.128 .OR. NTOTAL.EQ.256 .OR. 
+ NTOTAL.EQ.512 .OR. NTOTAL.EQ.1024) GO TO 245
WRITE (6,242) NTOTAL
FLAG=99
242 FORMAT(' NTOTAL = ',15.' AND IS NOT 64,128,256,512 OR 1024')
IF (NMAX.LE.NTOTAL) GO TO 251
WRITE (6,248) NMAX,NTOTAL
FLAG=99
248 FORMAT(' NMAX =',15,' -GT. NTOTAL =',15)
IF (NPAR.GE.0.AND.NPAR.LE.3) GO TO 263
WRITE (6,260) NPAR
FLAG=99
260 FORMAT(' CANNOT USE NPAR =M5)
IF (ESTMD.EQ.0 .OR. ESTMD.EQ.L) GO TO 269
WRITE (6,266) ESTMD
FLAG=99
266 FORMAT(' CAN NOT USE ESTMD =',I5)
IF (ESTMT.EQ.0 .OR. ESTMT.EQ.I) GO TO 275
WRITE (6,272) ESTMT
FLAG=99
272 FORMAT(' CAN NOT USE ESTMT =',I5)
IF(IFORCE.GE.0.AND.IFORCE.LE.2) GO TO 281
WRITE (6,278) IFORCE
FLAG=99
278 FORMAT(' CAN NOT USE IFORCE =',I5)
IF (NPAR.NE.3) GO TO 291
IF (IFORCE.EQ.1) GO TO 291
WRITE (6,283)
283 FORMAT(' ', 'MUST USE IF0RCE=1 WHEN NPAR=3')
FLAG=99
C MODIFY DATA: YERT-EXPERIMENTAL DATA, YEMT-MODIFIED EXPERIMENTAL DATA
291 IF (FLAG.NE.0) GO TO 999
CALL BASELN(YERT, NTOTAL, NBASE, IY(3))
NMAX=-1*NMAX
CALL DATMOD(YERT, NTOTAL, NBASE, NSMTH, NMAX, DTDATA, DT, PMAX, FLAG, IY)
NMAX=-1*NMAX
CALL DATMOD(YEMT, NTOTAL, NBASE, NSMTH, NMAX, DTDATA, DT, PMAX, FLAG, IY)
IF (FLAG.NE.0) GO TO 999
N=NMAX
C INITIALIZE CONSTANTS
VSBFU=30.E0
VSBFL=30.E0
VSBFLS=30.E0
VGCV=0.1975E0
ND2=N/2
N1=ND2+1
N2=ND2+2
FN=FLOAT(N)
PI=ARCOS(-1.E0)
AREA=PI*DIA**2/4.E0
LVU=LRING-LCONE-L
LVUM=FRACTM*LVU
LVUD=(1.E0-FRACTM)*LVU
VU=VCONE+AREA*LVUM
FU=VSBFU/TFU
FL=VSBFL/TFL
IF (SPLIT.EQ.0) GO TO 297
FLS=VSBFLS/TFLS
FLTCD=FL
FL=FLS+FLTCD
297 VINJ=VGCV+VL00P
M2=AREA*SQRTPOR
M4=M2**2
M5=L*SQRTPOR
M6=SQRTPD1*POR1
M7=FU*M2
TO=FN*DT
TINJ=VINJ/FU
C INITIALIZE VALUES OF S-LT VARIABLE
DO 300 I=1,N1
S(I)=CMPLX(0.E0,-2*PI*(I-1)/T0)
S12(I)=CSQRT(S(I))
300 M1(I)=M5*S12(I)
SN1=SQRTPOR1/D1*LVUD
DO 302 I=2,N1
ZN1=S12(I)*SN1
EP=CEXP(ZN1)
EM=CEXP(-ZN1)
CCOSH = (EP + EM) / 2.0
CSINH = (EP - EM) / 2.0
CC1(I) = (AREA*M6*(VLS(I) + FL)*CSINH + (VU*VL*S(I) + S12(I) + (VU*FL + VU*FL/FU)*S12(I) + (AREA*M6*S12(I) + CCOSH)/M7
CC2(I) = (AREA*POR/M6*(VU+S(I) + FU)*CSINH + M4*S12(I) + CCOSH)/M7
CC3(I) = (VU*VL*SQRT(POR) /M6*(S(I) + S12(I) + (AREA*M2*M6 + SQRT(POR) + 3/2*(VU*FL + VU*VL) + S12(I) + FU*FL*SQRT(POR) /M6/S12(I)) * CSINH

TRANSFORM EXPERIMENTAL DATA TO FREQ. DOMAIN.
DIRECT = +1, DATA IS FAST FOURIER TRANSFORMED
DIRECT = -1, DATA IS INVERTED
'DT' IS SENT TO SCALE THE FFT SO IT MATCHES THE LT
DO 301 I = 1, N
  YEMF(I) = CMPLX(YEMT(I), 0.0)
  DIRECT = 1
  CALL FFT(YEMF, N, DIRECT, DT)
  IF (IFORCE.LT.2) GO TO 309
  AMPB = AMPB*AMPB
  DO 307 I = 1, NTOTAL
    XEMT(I) = XERT(I)
    CALL BASELN(XERT, NTOTAL, NBASEB, IR(3))
    NMAX = -1*NMAX
    CALL DATMOD(XERT, NTOTAL, NBASEB, NSMTHB, NMAX, DTDATA, DT, PMAXB,
                +FLAG, IR)
    NMAX = -1*NMAX
    CALL DATMOD(XEMT, NTOTAL, NBASEB, NSMTHB, NMAX, DTDATA, DT, PMAXB,
                +FLAG, IR)
    IF (FLAG.NE.0) GO TO 999
    CALL MOMCS(XERT, NDATA, DTDATA, MOMRAW)
    CALL MOMADJ(MOMRAW, TLAGD)
    CALL MOMCS(YEMT, IY(3), DT, MOMMOD)
    CALL MOMADJ(MOMMOD, TLAGD)
  DO 308 I = 1, J
    XEMT(I) = XEMT(I) / MOMXEM(I)
    IF (AMPB.EQ.0) GO TO 309
    SF = ATN2(AMPB*ATND*RESB/FLOAT(AMPB*ATND*RESB)
    GO TO 311
  SF = 0.0
C
C INITIALIZE ITERATION PARAMETERS.
C IF ESTMD = 0, ESTIMATE D FROM FIRST MOMENT CALCULATION
C = 1, USE THE VALUE OF D READ IN AS THE INITIAL ESTIMATE
C IF ESTMT = 0, ESTIMATE TLAD FROM VOLUMES AND FLOW RATES
C = 1, USE THE VALUE OF TLAD READ IN AS THE INITIAL ESTIMATE
311 IF (ESTMT.NE.0) GO TO 313
    TLAGD = VDU/FU + VDL/FL
    IF (SPLIT.NE.0) TLAGD = TLAGD + VDLTCD/FLTCD
    TLAGM = TLAGD + TINJ/2.0
313 CALL MOMCS(YERT, NDATA, DTDATA, MOMRAW)
CALL MOMADJ(MOMRAW, TLAGD)
CALL MOMCS(YEMT, IY(3), DT, MOMMOD)
CALL MOMADJ(MOMMOD, TLAGD)
IF (ESTMD.NE.0) GO TO 315

\[ K = \text{MOMMOD}(h) - \text{TINJ}/2.E0 \]

\[ C1 = \text{AREA} \times (K1 \times (FU+FL) - \text{AREA} \times L \times PCR - VU - VL) \]

\[ C2 = L \times (K1 \times (FU+FL) - \text{AREA} \times L \times POR \times (FU+FL) / 2.E0 - VU - FL - VL \times FU) \]

\[ C3 = -L \times 3 \times POR \times FU \times FL / 6.E0 \]

\[ D = (-C2 + \sqrt{C2^2 - 4.E0 \times C1 \times C3}) / (2.E0 \times C1) \]

315 \[ \text{PAR}(1) = 1.E0 / \text{SQRT}(D) \]

\[ \text{PAR}(2) = \text{TLAGD} \]

\[ \text{PAR}(3) = \text{TPULSE} \]

\[ \text{PAR1} = \text{PAR}(1) \]

\[ \text{PAR2} = \text{PAR}(2) \]

C \[ \text{PAR}(1) \] \text{ARE THE INITIAL VALUES OF THE ITERATION PARAMETERS \n
C \[ \text{NEWPAR}(1) \] \text{WILL BE THE ITERATED VALUES OF THE PARAMETERS} \n
DO 317 I = 1, 3

317 NEWPAR(I) = PAR(I)

C

C IF NEVQL = 0, THE PROGRAM READS IN VALUES OF D, TLAG, AND TPULSE \n
C AND CALCULATES SSQRW FOR THESE VALUES USING THE PREVIOUSLY SET \n
C VALUES OF NPAR, IFORCE, ETC. \n
IF (NEVAL.EQ.0) GO TO 316

WRITE (6,1)

WRITE(6,5000)


ICALL = 0

DO 6000 I = 1, NEVAL

READ (5,5020) D, TLAGD, TPULSE

5020 FORMAT (E14.7, 2E16.7)

PAR1 = 1.E0 / SQRT(D)

PAR2 = TLAGD

CALL LAPTR(ESOLN, SCALE, SSQRW)

WRITE (6, 5050) D, PAR1, TLAGD, TPULSE, SSQRW

5050 FORMAT (' ', E14.7, 4E16.7)

6000 CONTINUE

GO TO 999

316 ICALL = 0

C \THE IMSL ROUTINE ZXMIN APPLIES A QUASI-NEWTON METHOD TO FIND THE \n
C \MINIMUM OF A FUNCTION. THE PROCEDURE STOPS WHEN THE \n
C ITERATION PARAMETER DIGITS MATCH TO 'NSIG' DIGITS. \n
IF (NPAR.EQ.0) GO TO 318

CALL ZXMIN(FUNCT, NPAR, NSIG, KMAX, I OPT, NEWPAR, HESSN, GRADNT, \n
+SSQRW, WORK, FLAG)

C \SKIP A PAGE FOR THE PRINTING OF OUTPUT \n
318 WRITE (6,1)

1 FORMAT ('1', ' ')

C

C \FLAG IS AN ERROR INDICATOR. \n
IF (FLAG.EQ.0) GO TO 325

IF (FLAG.NE.131) GO TO 319

WRITE (6,3) KMAX
FORMAT(' ', 'NSIG NOT REACHED IN', 14, ' FUNCTION CALLS')
GO TO 323
319 IF (FLAG.NE.130) GO TO 321
WRITE (6, 5)
5 FORMAT(' ', 'ITERATIONS STOPPED DUE TO ROUNDING ERRORS',
       ' IN ZXMIN ROUTINE')
GO TO 323
321 WRITE (6, 7)
7 FORMAT(' ', 'HESSIAN MATRIX IS NOT POSITIVE DEFINITE')
323 WRITE (6, 9)
9 FORMAT(' ', 'THE LAST RESULTS ARE LISTED BELOW')
C
C DNEW IS THE ITERATED ESTIMATE OF D
325 DNEW=1.E0/NEWPAR (1)**2
   TLAGDN=NEWPAR (2)
   IF (NPAR.EQ.3) TPULSE=NEWPAR (3)
C INVERT SOLUTION TO COMPARE TO EXPERIMENTAL RESULTS
   PAR1=NEWPAR (1)
   PAR2=NEWPAR (2)
   CALL LAPTR (ESOLN, SCALE, SSQRW)
   DO 342 I=2, ND2
342 ESOLN (N+2-I)=CONJG (ESOLN (I))
   DIRECT=-1
   CALL FFT (ESOLN, N, DIRECT, DT)
   SSQR=O.E0
   DO 344 I=1, N
   TIME (I)=((I-1)*DT
   YMODEL (I)=REAL (ESOLN (I))
344 SSQR=SSQR+((YEMT (I)-YMODEL (I))**2
C CALCULATE MOMENTS FOR THE MODIFIED DATA THAT IS SHIFTED BY THE
C NEWLY CALCULATED LAG-TIME AND ALSO FOR THE PREDICTED VALUES:
C MOMSFT (I) AND MOMPRD (I), RESPECTIVELY.
   DO 348 I=1, 6
348 MOMSFT (I)=MOMMOD (I)
   T1=TLAGDN-TLAGD
   CALL MOMADJ (MOMSFT, T1)
   CALL MOMCS (YMODEL, N, DT, MOMPRD)
   CALL MOMADJ (MOMPRD, TLAGDN)
C CALCULATE OTHER VALUES FOR PRINTING.
   K1=AREA*DNEW/(L*FU)
   K2=K1*FU/FL
   KE=POR1/POR
   KD=D1/DNEW
   KL=LVUD/L
   TAU1=VU/FU
   TAU2=VL/FL
   H1=TAU1*DNEW/(L*VU)
   H2=TAU2*DNEW/(L*VU)
   B=SQRT(L**2*POR/DNEW)
C CALCULATE THEORETICAL MOMENTS
$T_4 = 1.0 + K_1 + K_2 + K_L / K_D$

$MOMTHR(1) = K_2 / T_4 * SCALE$

$MOMTHR(4) = 6 * K_1 * K_2 / (1.0 + K_1 + K_2) + 3 * (K_1 * K_2) * (1.0 + K_1 + K_2) + 6 * K_1 * K_2 / (1.0 + K_1 + K_2) + 1.0 + K_1 + K_2 / K_D / (1.0 + K_1 + K_2) / (K_D * K_L) / (K_E * K_L + 1.0) + 1.0 + K_1 + K_2 / K_D$

$MOMTHR(4) = TAU_1 * (1.0 + K_1 + K_2 / K_D) + TAU_2 * T_4$

$T_1 = 12 * (K_1 * K_2) * T_4 + 10 * K_1 * K_2 / (1.0 + K_1 + K_2) + 2.5 * (K_1 * K_2) + 1.4 * (1.0 + K_1 + K_2) / 3.0$

$T_2 = TAU_1 * (K_2 * T_4 + 1.0 + 4 * K_1) + 5 * K_1 * K_2 / (5.0 + 4 * K_2 + 1.0) / 3.0$

$T_3 = TAU_1 * (K_2 / (1.0 + K_1 + K_2) + 2 * TAU_1 + TAU_2 * (1.0 + K_1 + K_2 + 2 * K_1 * K_2) + 4 * TAU_2^2 / (1.0 + K_1 + K_2) / 2$

$MOMTHR(3) = 6 * T_1 / (6.0 + T_1 + B * T_4 + T_3)$

$MOMTHR(5) = MOMTHR(3) / MOMTHR(1)$

$MOMTHR(6) = MOMTHR(5) / MOMTHR(4) / 2$

C CORRECT THEORETICAL MOMENTS FOR DIFFERENT FORCING FUNCTIONS

IF (IFORCE.EQ.0) TPULSE = (NSQRWV-1) * DT

T1 = -TPULSE / FLOAT(2)

IF (IFORCE.EQ.0.OR.IFORCE.EQ.1) CALL MOMADJ(MOMTHR,T1)

IF (IFORCE.EQ.2) CALL MOMADJ(MOMTHR, -MOMXEM(4))

C *****************************************************

C PRINT OUT RESULTS.

WRITE (6,21)

21 FORMAT('0', 'QUASI-NEWTON MINIMIZATION OF SUM-OF-SQUARES')

WRITE (6,23)

23 FORMAT('1', 'IN THE FREQUENCY DOMAIN. PROGRAM: ZXMINW7')

IF (NPAR.EQ.0) GO TO 353

WRITE (6,25)

25 FORMAT('0', 'ITERATION PARAMETERS: D (EFF. DIFF.)')

IF (NPAR.EQ.1) GO TO 353

WRITE (6,26)

26 FORMAT('0', 'TLAG (LAG-TIME)')

IF (NPAR.EQ.2) GO TO 353

WRITE (6,27)

27 FORMAT('0', 'TPULSE (SQUARE WAVE PULSE', 'TIME)')

353 WRITE (6,29) NRUN, N, DT, NPLT

29 FORMAT('0', 'RUN#', 14, 3X, 'N=' , 14, ' POINTS DT=', F7.5, ' SECONDS PELLET #', 15)

IF (IFORCE=1) 354, 356, 358

WRITE (6,31)

31 FORMAT('0', 'FORCING FUNCTION = DISCRETE SQUARE WAVE')

WRITE (6,33) NSQRWV

33 FORMAT('0', '19X', 'NSQRWV = ', 14)

GO TO 361

356 WRITE (6,35)

35 FORMAT('0', 'FORCING FUNCTION = ANALYTICAL SQUARE WAVE')

WRITE (6,37) TPULSE
FORMAT(' ',19X,'PULSE TIME =',F9.5,' SECONDS')
GO TO 361
358 WRITE (6,39) NBYPAS
39 FORMAT('O','FORCING FUNCTION = BYPASS RUN #',I5)
WRITE (6,41) ATNB,AMPB,RESB
41 FORMAT(' ',ATNB=' ',AMPB=' ',RESB=' ',
+15,'=')
WRITE (6,10) NSMTHB
10 FORMAT(' ',NUMBER OF DATA SMOOTHINGS =',I7)
WRITE (6,11) NBASEB
11 FORMAT(' ',NUMBER OF BASELINE POINTS =',I7)
C1=PMAXB
IF (PMAXB.CT.1000.E0) C1=PMAXB-1000.E0
IF (C1.LT.500.E0) GO TO 359
WRITE(6,12) PMAXB
12 FORMAT(' ',PMAX- TRUNCATION PERCENT =',F13.5)
GO TO 360
359 WRITE (6,13) PMAXB
13 FORMAT(' ',PMAX- FIXED TRUNCATION TIME =',F13.5,' SECONDS')
360 T1=IR(1)*DT
T2=(IR(2)-1)*DT
T3=(IR(3)-1)*DT
T4=(IR(4)-1)*DT
WRITE (6,14) T1
14 FORMAT(' ',DATA ZEROED BEFORE =',F13.5,' SECONDS')
WRITE (6,15) T2
15 FORMAT(' ',PEAK MAXIMUM =',F13.5,' SECONDS')
WRITE (6,16) T3
16 FORMAT(' ',DATA ZEROED AFTER =',F13.5,' SECONDS')
WRITE (6,17) T4
17 FORMAT(' ',TOTAL DURATION OF RESPONSE =',F13.5,' SECONDS')
WRITE (6,18) XEMT(IR(2))
18 FORMAT(' ',VALUE OF PEAK MAXIMUM =',F13.5)
WRITE (6,19) MOMXEM(1),MOMXEM(2),MOMXEM(3)
19 FORMAT(' ',MO =',F14.6,' M1 =',F14.6,' M2 =',F14.6)
WRITE (6,20) MOMXEM(4),MOMXEM(5),MOMXEM(6)
20 FORMAT(' ',U1 =',F14.6,' U2 =',F14.6,' U2C =',F14.6)
361 WRITE (6,43)
43 FORMAT('O','EXPERIMENTAL DATA:')
WRITE (6,45) ATND,AMPD,RESD,SPLIT
45 FORMAT(' ',ATND=',I5,' AMPD=',I5,' RESD=',I5,
+15,' SPLIT=',I5)
WRITE (6,47) FU,FL,VCONE,VL
47 FORMAT(' ',FU=',F9.3,' FL=',F9.3,' VCONE=',F9.3,
+',' VL=',F9.3)
WRITE (6,49) VDU,VDL,VLOOP,VINJ
49 FORMAT(' ',VDU=',F9.3,' VDL=',F9.3,' VLOOP=',F9.3,
+',' VINJ=',F9.3)
IF (SPLIT.NE.0) WRITE (6,50) FLS,FLTCD,VDLTC,TAUTC
50 FORMAT(' ',FLS=',F9.3,' FLTCD=',F9.3,' VDLTC=',F9.3,
+',' TAUTC=',F9.3)
WRITE (6, 51) LRING, L, LCONE, LVU
               'LVU=', F9.3)
WRITE (6, 53) DIA, AREA, POR, POR1
               'POR1=', F9.3)
WRITE (6, 54) FRACTM, LVUM, VU, LVUD
               'LVUD=', F9.3)
WRITE (6, 55) TAU1, TAU2, TINJ, D1
      FORMAT (1X, 'TAU1=', F9.6, 'TAU2=', F9.6, 'TINJ=', F9.3, +
               '+D1=', F9.3)
WRITE (6, 57)
      IF (ESTMD .LT. 1) 364, 366, 370
WRITE (6, 59) D
      FORMAT ('INITIAL D:', E14.6) (FROM FIRST MOMENT)
GO TO 370
WRITE (6, 61) D
      FORMAT ('INITIAL D:', E14.6) (FROM INPUT DATA)
WRITE (6, 65) DNEW
      FORMAT (1X, 'FINAL D:', E14.6)
C1 = (DNEW - D) / DNEW * 100.E0
WRITE (6, 67) C1
WRITE (6, 69) TLAGM
      FORMAT ('TLAGM:', F12.4) (FROM VOLUMES AND

Go To 378
WRITE (6, 71) TLAGD
      FORMAT ('TLAGD:', F12.4) (FROM INPUT DATA)
IF (IForce .NE. 2) WRITE (6, 75) TLAGDN
WRITE (6, 77) C3
WRITE (6, 84) C3
WRITE (6, 86) NEWPAR (3)
      FORMAT (1X, 'NEWPAR (3):', F12.4)
WRITE (6, 88) TLAGB
      FORMAT ('TLAGB:', F12.4)
C2 = (TLAGDN - TLAGD) / TLAGDN * 100.E0
WRITE (6, 77) C2
WRITE (6, 79) TLAGD + TINJ / 2
      FORMAT ('TLAGD+TINJ/2:', F12.4)
WRITE (6, 80) C3
WRITE (6, 82)
      IF (NPAR .NE. 3) GO TO 90
C3 = (NEWPAR (3) - PAR (3)) / NEWPAR (3) * 100.E0
WRITE (6, 80) PAR (3)
WRITE (6, 84) C3
WRITE (6, 86) NEWPAR (3)
      FORMAT (1X, 'NEWPAR (3):', F12.4)
WRITE (6, 88) TLAGB
      FORMAT ('TLAGB:', F12.4)
C2 = (TLAGDN - TLAGD) / TLAGDN * 100.E0
WRITE (6, 77) C2
WRITE (6, 79) TLAGD + TINJ / 2
      FORMAT ('TLAGD+TINJ/2:', F12.4)
WRITE (6, 80) C3
WRITE (6, 82)
WRITE (6, 81) K1, K2, H1, H2
FORMAT ('0', ' K1=', F9.6, ' K2=', F9.6, ' H1=', F9.6, + ' H2=', F9.6)
WRITE (6, 87)
FORMAT ('0', 'STATISTICS:')
WRITE (6, 89) NSMTH
FORMAT ('0', 'NUMBER OF DATA SMOOTHINGS :', I7)
WRITE (6, 91) NBASE
FORMAT ('0', 'NUMBER OF BASELINE POINTS :', I7)
CLPMAX
IF (PMAX.GT.1000.E0) C1=PMAX-1000.E0
IF (C1.LT.500.E0) GO TO 380
WRITE (6, 93) PMAX
FORMAT ('0', 'PMAX- TRUNCATION PERCENT :', F13.5)
GO TO 382
380 WRITE (6, 95) PMAX
FORMAT ('0', 'PMAX- FIXED TRUNCATION TIME:', F13.5, ' SECONDS')
382 T1=IY(1)*DT
T2=(IY(2)-1)*DT
T3=(IY(3)-1)*DT
T4=(IY(4)-1)*DT
WRITE (6, 97) T1
FORMAT ('0', 'DATA ZEROED BEFORE :', F13.5, ' SECONDS')
WRITE (6, 98) T2
FORMAT ('0', 'PEAK MAXIMUM :', F13.5, ' SECONDS')
WRITE (6, 99) T3
FORMAT ('0', 'DATA ZEROED AFTER :', F13.5, ' SECONDS')
WRITE (6, 100) T4
FORMAT ('0', 'TOTAL DURATION OF RESPONSE :', F13.5, ' SECONDS')
WRITE (6, 101) WORK(3)
FORMAT ('0', 'SIGNIFICANT DIGITS IN SOLN.:', F13.5)
WRITE (6, 102) WORK(2)
FORMAT ('0', 'NUMBER OF FUNCTION CALLS :', F8.0)
WRITE (6, 103) SSQR
FORMAT ('0', 'SUM-OF-SQUARES TIME:', 8X, ':', F13.5)
WRITE (6, 104) YEMT(IY(2))
IF (NPAR.EQ.0) GO TO 106
WRITE (6, 105) WORK(3)
FORMAT ('0', 'SSQRW=SSQR/WN/DT/DT')
WRITE (6, 106) SSQRW
FORMAT ('0', 'FREQ. SCALED:', F13.5)
C1=SQRT (SSQR/FLOAT(N-1))
WRITE (6, 107) C1
FORMAT ('0', 'STD DEV/PEAK MAX*100 :', F13.5)
IF (SF.NE.O.E0) GO TO 384
WRITE (6,113) SCALE
113 FORMAT(' ', 'M * TCD CONSTANT / ATND : ', F13.5)
   GO TO 386
384 WRITE (6,115) SCALE
115 FORMAT(' ', 'SCALE FACTOR', 15X, ': ', F13.5)
386 WRITE (6,117)
117 FORMAT('0', 25X, 'CUBIC SPLINE MOMENTS', 17X, 'THEORETICAL')
   WRITE (6,119)
119 FORMAT(' ', 7X, 'RAW DATA', 6X, 'MOD DATA', 6X, 'MOD+SHIFT', 5X,
   'SSQR DATA', 5X, 'EQUATIONS')
   WRITE (6,121) MOMRAW(1), MOMMOD(1), MOMSFT(1), MOMPRD(1), MOMTHR(1)
121 FORMAT(' ', 5F14.6)
   WRITE (6,123) MOMRAW(2), MOMMOD(2), MOMSFT(2), MOMPRD(2), MOMTHR(2)
123 FORMAT(' ', 5F14.6)
   WRITE (6,125) MOMRAW(3), MOMMOD(3), MOMSFT(3), MOMPRD(3), MOMTHR(3)
125 FORMAT(' ', 5F14.6)
   WRITE (6,127) MOMRAW(4), MOMMOD(4), MOMSFT(4), MOMPRD(4), MOMTHR(4)
127 FORMAT(' ', 5F14.6)
   WRITE (6,129) MOMRAW(5), MOMMOD(5), MOMSFT(5), MOMPRD(5), MOMTHR(5)
129 FORMAT(' ', 5F14.6)
   WRITE (6,131) MOMRAW(6), MOMMOD(6), MOMSFT(6), MOMPRD(6), MOMTHR(6)
131 FORMAT(' ', 5F14.6)
   IF (OUTPRT.NE.1) GO TO 141
   WRITE (6,135)
135 FORMAT('0', 13X, 'FORCING FUNCTION EXPERIMENTAL DATA MODELING',
   1 ' RESULTS')
   WRITE (6,137)
137 FORMAT('0', 13X, 'TIME RAW MOD RAW MOD',
   1 ' REAL IMAG')
   DO 390 I=1,N
   C1=XEMT(I)
   IF (IFORCE.EQ.2) C1=XERT(I)
   C2=AIMAG(SOLN(I))
390 WRITE (6,139) I, TIME(I), C1, XEMT(I), YERT(I), YEMT(I), YMODEL(I), C2
   IF (NPAR.EQ.0) GO TO 151
   WRITE (6,143) IOPT
143 FORMAT('0', 'FINAL SYSTEM OF EQUATIONS SOLVED USING IOPT =', I3)
   IF (NPAR.NE.2) 140, 146, 147
140 WRITE (6,142) HESSN(1), GRADNT(1)
142 FORMAT(' ', 13F14.7, F20.7)
   GO TO 151
146 WRITE (6,145) HESSN(1), HESSN(2), GRADNT(1)
   WRITE (6,145) HESSN(2), HESSN(3), GRADNT(2)
145 FORMAT(' ', 2F14.7, F20.7)
   GO TO 151
147 WRITE (6,149) HESSN(1), HESSN(2), HESSN(3), GRADNT(1)
   WRITE (6,149) HESSN(2), HESSN(4), HESSN(5), GRADNT(2)
   WRITE (6,149) HESSN(3), HESSN(5), HESSN(6), GRADNT(3)
149 FORMAT(' ', 3F14.7, F20.7)
151 IF (FLAG.NE.0) GO TO 999
C IF '0UTMOD'=1, THE YEMT VALUES ARE PRINTED TO LUN #13
C IF '0UTMIN'=1, THE YMODEL VALUES ARE PRINTED TO LUN #14
C IF (OUTMOD.NE.1) GO TO 395
WRITE (13, 214) NRUN
WRITE (13, 214) N
DO 394 I=1,N
394 WRITE (13, 218) YEMT (I)
395 IF (OUTMIN.NE.1) GO TO 999
WRITE (14, 214) NRUN
WRITE (14, 214) N
DO 397 I=1,N
397 WRITE (14, 218) YMODEL (I)
C ********************************************************************************************************
999 STOP
C END
C SUBROUTINE DATMOD(Y,N,NBASE,NSMTH,NMAX,DTDATA,DT,PMAX,FLAG,LY)
INTEGER I, J, N, NBASE, NSMTH, NMAX, NMAXR, FLAG, ILEAD, ITAIL
INTEGER ITOLD, ITNEW, ISMTH, IY (4)
REAL Y (N), MAX, DT, PMAX, PMAXR, WKOLD(1024), WKNEW(1024), AVE
FLAG=0
C IF NMAX<0, DATA SET IS ONLY TRUNCATED TO NMAX DATA POINTS
NMAXR=NMAX
IF (NMAXR.LT.0) GO TO 207
IF (PMAX.LT.1000.E0) GO TO 100
PMAXR=PMAX-1000.E0
GO TO 105
100 PMAXR=PMAX
105 IF (NBASE.LE.1000) GO TO 106
NBASE=R-NBASE-1000
GO TO 107
106 NBASE=R-NBASE
107 IF (NSMTH.GT.1) GO TO 165
C IF NSMTH<0, SMOOTH DATA UNTIL CONSTANT TRUNCATION TIME IS
C OBTAINED, UP TO ABS(NSMTH) TIMES
IF (PMAXR.GT.500.E0) GO TO 115
FLAG=99
WRITE (6, 109) PMAX, NSMTH
109 FORMAT (' ', 'PMAX =', F9.4, ' NSMTH =', I5)
WRITE (6, 110)
110 FORMAT (' ', 'CAN NOT VARY TRUNCATION TIME WHEN ITS VALUE IS'
+, ' FIXED')
GO TO 99
115 ISMTH=1
ITOLD=1
120 DO 125 I=1,N
WKOLD (I)=Y (I)
wKNEW (I)=Y (I)
170 CALL SMOOTH(WKNEW,N)
  DO 135 1=1,N
       Y(I)=WKOLD(I)
135 WKOLD(I)=WKNEW(I)
  CALL BASELN(WKNEW,N,NBASER,ITAIL)
  CALL MAXUM(WKNEW,N,IMAX)
  CALL TRUNCP(WKNEW,N,DTDATA,PMAXR,IMAX,ITNEW)
  IF (ITNEW.EQ.ITOLD) GO TO 145
  IF (ISMTH.EQ.(-1*NSMTH)) GO TO 150
       ISMTH=ISMTH+1
       ITOLD=ITNEW
  DO 140 1=1,N
140 WKNEW(I)=WKOLD(I)
  GO TO 130
145 NSMTH=-(ISMTH-1)
  GO TO 175
150 NSMTH=-100+NSMTH
  DO 155 1=1,N
155 Y(I)=WKOLD(I)
  GO TO 175
165 IF (NSMTH.EQ.0) GO TO 175
  DO 170 1=1,NSMTH
170 CALL SMOOTH(Y,N)
175 CALL BASELN(Y,N,NBASER,ITAIL)
  CALL MAXUM(Y,N,IMAX)
  CALL TRUNCP(Y,N,DTDATA,PMAXR,IMAX,ITAIL)
  IF (NBASER.GT.1000) CALL BASELN(Y,N,NBASE,ITAIL)
180 IF (PMAX.LT.1000.E0) GO TO 190
       IF (ITAIL.GT.(N-4)) ITAIL=N-4
       J=ITAIL
       AVE=59*Y(J)+54*(Y(J+1)+Y(J-1))+39*(Y(J+2)+Y(J-2))
++14*(Y(J+3)+Y(J-3))-21*(Y(J+4)+Y(J-4))
       Y(J)=AVE/231.E0
  DO 185 1=1,ITAIL
185 Y(I)=Y(I)-Y(J)
C ZERO TRAILING DATA VALUES
190 DO 195 I=ITAIL,N
195 Y(I)=0.E0
C REMOVE PRESSURE SPIKE FROM BEGINNING OF DATA
200 CALL SPIKE(Y,N,IMAX,ILEAD)
  IF (ILEAD.EQ.0) GO TO 210
  DO 205 I=1,ILEAD
205 Y(I)=0.E0
C RETAIN ONLY NMAX DATA POINTS AND CHANGE DT TO CORRESPOND TO NMAX
207 IF (NMAXR.LT.0) NMAX=-1*NMAX
  IF (NMAX.EQ.N.AND.NMAXR.LT.0) GO TO 235
210 M=N/FLOAT(NMAX)+0.5
  IF (M.EQ.1) GO TO 225
       J=0
  DO 215 I=1,N,M
J=J+1
Y(J)=Y(1)
IF (NMAXR.LT.O) GO TO 235

DT=M*DTHDATA
CALL MAXUM(Y,NMAX,IMAX)
CALL TRUNCP(Y,NMAX,DT,PMAXR,IMAX,ITAIL)
CALL SPIKE(Y,NMAX,IMAX,ILEAD)
IY(1)=ILEAD
IY(2)=IMAX
IY(3)=ITAIL
IY(4)=ITAIL-ILEAD
GO TO 99

NMAX=-1*NMAX

RETURN

END

C

SUBROUTINE SMOOTH(Y,N)
INTEGER I,J,K,K1,M
REAL Y(N) ,YP(9) ,SUM,YT(8)
DO 50 1=1,4
YT(I)=Y(I)
50 YT(I+4)=Y(N-4+I)
M=N-8
DO 100 1=2,9
J=I-1
100 YP(I)=Y(J)
DO 200 1=1,M
J=I+8
DO 150 K=1,8
K1=K+1
150 YP(K)=YP(K1)
YP(9)=Y(J)
SUM=59*YP(5)+54*(YP(4)+YP(6))+39*(YP(3)+YP(7))+14*(YP(2)+YP(8))-21*(YP(1)+YP(9))
Y(I)=SUM/231.0
200 CONTINUE
DO 210 1=1,M
210 Y(N-1-I)=Y(N-1-7)
DO 220 1=1,4
Y(I)=YT(I)
220 Y(N-4+I)=YT(1+4)
RETURN

END

C

SUBROUTINE BASELN(Y,N,NBASE,ITAIL)
INTEGER I,ITAIL,N,NBASE,IBASE,J
REAL Y(N) ,BASE
IF (NBASE.NE.0) GO TO 5
WRITE (6,2) NBASE
2 FORMAT(' ', 'WARNING: NBASE=0 AND NO SHIFTING IS DONE')
GO TO 99
5 IF (NBASE.GT.0) GO TO 10
  IBASE=-1*NBASE
  IF (IBASE.LE.N) GO TO 8
    WRITE (6,6) IBASE,N
6  FORMAT(' ', 'WARNING: IBASE=', I4, ' .GT. N=', I4)
   WRITE (6,7)
7  FORMAT(' ', 'IBASE SET EQUAL TO N')
   IBASE=N
8  J=0
   GO TO 30
10 IF (NBASE.GT.1000) GO TO 20
   IBASE=NBASE
   IF (IBASE.LE.N) GO TO 15
     WRITE (6,16) IBASE,N
16  FORMAT(' ', 'WARNING: IBASE=', I4, ' .GT. N=', I4)
17  FORMAT(' ', 'IBASE SET EQUAL TO N')
     IBASE=N
15  J=N-IBASE
     GO TO 30
20 IF (ITAIL.LE.N) GO TO 25
     WRITE (6,21) ITAIL,N
21  FORMAT(' ', 'WARNING: ITAIL=', I4, ' .GT. N=', I4)
23  FORMAT(' ', 'ITAIL SET EQUAL TO N')
25  IBASE=NBASE-1000
   IF ((ITAIL+IBASE).LE.N) GO TO 29
     J=ITAIL+IBASE
     WRITE (6,26) J,N
26  FORMAT(' ', 'WARNING: ITAIL+IBASE=', I4, ' .GT. N=', I4)
27  FORMAT(' ', 'IBASE SET EQUAL TO N-ITAIL')
     IBASE=N-ITAIL
     IF (IBASE.GT.0) GO TO 29
     BASE=0.E0
     GO TO 45
29  J=ITAIL
30  BASE=0.E0
   DO 40 I=1,IBASE
30    BASE=BASE+Y(J+I)
40  DO 50 I=1,N
45  BASE=BASE/FLOAT(IBASE)
50  Y(I)=Y(I)-BASE
99 RETURN
C
SUBROUTINE MAXUM(Y,N,IMAX)
  INTEGER  I,N,IMAX
  REAL Y(N),MAX

\begin{verbatim}
MAX=Y(1)
IMAX=1
DO 10 I=1,N
  IF (Y(I) .LE. MAX) GO TO 10
  MAX=Y(I)
  IMAX=I
10 CONTINUE
RETURN
END

C SUBROUTINE TRUNCP(Y,N,DT,PMAXR,IMAX,ITAIL)
INTEGER I,IMAX,ITAIL,N,NM4,IFLAG
REAL Y(N),PMAXR,MAXC,DT,AVEC
IF (PMAXR.GT.500.E0) GO TO 20
ITAIL=INT(PMAXR/DT+1+.0001E0)
IF (ITAIL.LE.N) GO TO 199
  WRITE(6,10) ITAIL,N
10 FORMAT(' 'WARNING: ITAIL=',I4,' .GT. N=',I4)
  WRITE (6,11)
11 FORMAT(' ITAIL SET EQUAL TO N')
  ITAIL=N
  GO TO 199
20 MAXC=Y(IMAX)*(PMAXR-500.E0)/100.E0
IFLAG=0
ITAIL=N
NM4=N-4
DO 40 I=IMAX,NM4
  IF (Y(I).GT.MAXC.AND.IFLAG.EQ.0) GO TO 40
  IFLAG=1
  AVEC=59*Y(I)+54*(Y(I+1)+Y(I-1))+39*(Y(I+2)+Y(I-2))+14*(Y(I+3)+Y(I-3))-21*(Y(I+4)+Y(I-4))
  AVEC=AVEC/231.E0
  IF (AVEC.GT.MAXC) GO TO 40
  ITAIL=I
  GO TO 199
40 CONTINUE
199 RETURN
END

C SUBROUTINE SPIKE(Y,N,IMAX,I LEAD)
INTEGER I,J,N,IMAX,ILEAD
REAL Y(N)
ILEAD=0
DO 320 I=2,IMAX
  J=IMAX-I+1
  IF (Y(J).GT.0.E0) GO TO 300
    ILEAD=J
  GO TO 340
300 IF (Y(J).LT.Y(J+1)) GO TO 320
    ILEAD=J
320 CONTINUE
END
\end{verbatim}
IF (Y(J-1) .LT. Y(J)) GO TO 320
IF (Y(J) .GT. (Y(MAX) + .5)) GO TO 320
ILEAD = J
GO TO 340
CONTINUE
RETURN
END

SUBROUTINE FFT(X,N,DIRECT,DT)
INTEGER J1, J2, J3, J4, J5, J6, J7, J8, J9, J10, N, RADIX, L, L1, L2, K, J, NM1
INTEGER L2T2, NDL1, DIRECT, K1, K2
REAL PI, DT, FN, C1, C2
COMPLEX X(N), Y(1024), W

C THIS IS A MODIFIED VERSION OF THE 'FFT' SUBROUTINE WRITTEN AND
C USED BY BOB THIES. IT CAN BE USED TO CALCULATE THE FFT OF A
C REAL OR COMPLEX DATA SET CONTAINING 32, 64, 128, 256, 512 OR 1024 POINTS
PI = ARCOS (-1.0)
FN = FLOAT (N)
RADIX = ALOG(FN)/ALOG(2.0) + 0.5
IF (N.GT.128) GO TO 304
IF (N-64) 301, 302, 303
301 DO 310 J1 = 1, 2
DO 310 J2 = 1, 2
DO 310 J3 = 1, 2
DO 310 J4 = 1, 2
DO 310 J5 = 1, 2
310 Y((J5-1)+2*(J4-1)+4*(J3-1)+8*(J2-1)+16*(J1-1)+1) =
+X((J1-1)+2*(J2-1)+4*(J3-1)+8*(J4-1)+16*(J5-1)+1)
GO TO 309
302 DO 320 J1 = 1, 2
DO 320 J2 = 1, 2
DO 320 J3 = 1, 2
DO 320 J4 = 1, 2
DO 320 J5 = 1, 2
DO 320 J6 = 1, 2
320 Y((J6-1)+2*(J5-1)+4*(J4-1)+8*(J3-1)+16*(J2-1)+32*(J1-1)+1) =
+X((J1-1)+2*(J2-1)+4*(J3-1)+8*(J4-1)+16*(J5-1)+32*(J6-1)+1)
GO TO 309
303 DO 330 J1 = 1, 2
DO 330 J2 = 1, 2
DO 330 J3 = 1, 2
DO 330 J4 = 1, 2
DO 330 J5 = 1, 2
DO 330 J6 = 1, 2
DO 330 J7 = 1, 2
330 Y((J7-1)+2*(J6-1)+4*(J5-1)+8*(J4-1)+16*(J3-1)+32*(J2-1)+
+64*(J1-1)+1) = X((J1-1)+2*(J2-1)+4*(J3-1)+8*(J4-1)+16*(J5-1)+
+32*(J6-1)+64*(J7-1)+1)
GO TO 309
304 IF (N-512) 305, 306, 307
305 DO 335 J1 = 1, 2
   DO 335 J2 = 1, 2
   DO 335 J3 = 1, 2
   DO 335 J4 = 1, 2
   DO 335 J5 = 1, 2
   DO 335 J6 = 1, 2
   DO 335 J7 = 1, 2
   DO 335 J8 = 1, 2
335 Y ((J8-1) + 2*(J7-1) + 4*(J6-1) + 8*(J5-1) + 16*(J4-1) + 32*(J3-1) + 64*(J2-1) + 128*(J1-1) + 1) = X ((J1-1) + 2*(J2-1) + 4*(J3-1) + 8*(J4-1) + 16*(J5-1) + 32*(J6-1) + 64*(J7-1) + 128*(J8-1) + 1)
   GO TO 309
306 DO 340 J1 = 1, 2
   DO 340 J2 = 1, 2
   DO 340 J3 = 1, 2
   DO 340 J4 = 1, 2
   DO 340 J5 = 1, 2
   DO 340 J6 = 1, 2
   DO 340 J7 = 1, 2
   DO 340 J8 = 1, 2
   DO 340 J9 = 1, 2
340 K1 = (J9-1) + 2*(J8-1) + 4*(J7-1) + 8*(J6-1) + 16*(J5-1) + 32*(J4-1) + 64*(J3-1) + 128*(J2-1) + 256*(J1-1) + 1
   K2 = (J1-1) + 2*(J2-1) + 4*(J3-1) + 8*(J4-1) + 16*(J5-1) + 32*(J6-1) + 64*(J7-1) + 128*(J8-1) + 256*(J9-1) + 1
   Y (K1) = X (K2)
   GO TO 309
307 DO 345 J1 = 1, 2
   DO 345 J2 = 1, 2
   DO 345 J3 = 1, 2
   DO 345 J4 = 1, 2
   DO 345 J5 = 1, 2
   DO 345 J6 = 1, 2
   DO 345 J7 = 1, 2
   DO 345 J8 = 1, 2
   DO 345 J9 = 1, 2
   DO 345 J10 = 1, 2
345 K1 = (J10-1) + 2*(J9-1) + 4*(J8-1) + 8*(J7-1) + 16*(J6-1) + 32*(J5-1) + 64*(J4-1) + 128*(J3-1) + 256*(J2-1) + 512*(J1-1) + 1
   K2 = (J1-1) + 2*(J2-1) + 4*(J3-1) + 8*(J4-1) + 16*(J5-1) + 32*(J6-1) + 64*(J7-1) + 128*(J8-1) + 256*(J9-1) + 512*(J10-1) + 1
   Y (K1) = X (K2)
309 DO 360 L = 1, RADIX
   L1 = 2**(RADIX-L+1)
   L2 = 2**(L-1)
   L2T2 = L2*2
   NDL1 = N/L1
   DO 360 K = 1, N, NDL1
   W = CEXP (CMPLX (0, EO, DIRECT*PI*(J-1)*L1/FN))
Y (K+J-1) = Y (K+J-1) + Y (K+J+L2-1) \* W

Y (K+J+L2-1) = Y (K+J-1) - 2 \* Y (K+J+L2-1) \* W

IF (DIRECT.EQ.-1) GO TO 380

DO 370 I = 1, N

X (I) = Y (I) \* DT

GO TO 399

DO 380 I = 1, N

X (I) = Y (I) / FN / DT

RETURN

END

SUBROUTINE MOMADJ (MOM, TLAG)

REAL MOM (6), TLAG

C THIS SUBROUTINE SUBTRACTS TLAG FROM THE 1ST ABS. MOMENT AND

C ADJUSTS THE OTHER MOMENTS

MOM (4) = MOM (4) - TLAG

MOM (5) = MOM (6) + MOM (4) ** 2

MOM (2) = MOM (4) \* MOM (1)

MOM (3) = MOM (5) \* MOM (1)

RETURN

END

SUBROUTINE MOMCS (Y, N, DT, MOM)

INTEGER I, IER, IC, N

REAL Y (N), DT, MOM (6), TIME (1024), Z (1024), BPAR (4), C (1023, 3)

C THIS SUBROUTINE CALCULATES THE MOMENTS FOR THE DATA IN Y

C THE IMSL ROUTINE 'ICSICU' APPROXIMATES THE CURVE WITH CUBIC

C SPLINES. THE DERIVATIVES AT THE END-POINTS, BPAR (1), ARE SET

C EQUAL TO ZERO. THE IMSL ROUTINE 'DCSQDU' EVALUATES THE AREA

C UNDER THE CURVE USING THE SPLINE COEFFICIENTS GENERATED ABOVE.

C MOM (1-3) - ZEROOTH, FIRST AND SECOND MOMENTS

C MOM (4-5) - FIRST AND SECOND ABSOLUTE MOMENTS

C MOM (6) - SECOND-CENTRAL MOMENT

IC = N - 1

DO 410 I = 1, 4

BPAR (I) = 0.0

DO 420 I = 1, N

TIME (I) = (I - 1) \* DT

CALL ICSICU (TIME, Y, N, BPAR, C, IC, IER)

CALL DCSQDU (TIME, Y, N, C, IC, TIME (1), TIME (N), MOM (1), IER)

DO 430 I = 1, N

Z (I) = Y (I) \* TIME (I)

CALL ICSICU (TIME, Z, N, BPAR, C, IC, IER)

CALL DCSQDU (TIME, Z, N, C, IC, TIME (1), TIME (N), MOM (2), IER)

DO 440 I = 1, N

Z (I) = Y (I) \* TIME (I) ** 2

CALL ICSICU (TIME, Z, N, BPAR, C, IC, IER)

CALL DCSQDU (TIME, Z, N, C, IC, TIME (1), TIME (N), MOM (3), IER)

C CALCULATE OTHER MOMENTS

MOM (4) = MOM (2) / MOM (1)
MOM(5) = MOM(3)/MOM(1)  
MOM(6) = MOM(5) - MOM(4)*A2  
RETURN  
END  

C SUBROUTINE FUNCT(NPAR, NEWPAR, SSQRW)  
INTEGER NPAR  
REAL NEWPAR(NPAR), SCALE, SSQRW  
REAL FU, FL, VU, VL, AREA, L, POR, LVUD, D1, PAR1, PAR2, TPULSE, SF  
COMPLEX*8 CMODEL(1024)  
COMMON/REELS/FU, FL, VU, VL, AREA, L, POR, LVUD, D1, PAR1, PAR2, TPULSE, SF  
IF (NPAR.GE.1) PAR1 = NEWPAR(1)  
IF (NPAR.GE.2) PAR2 = NEWPAR(2)  
IF (NPAR.GE.3) TPULSE = NEWPAR(3)  
CALL LAPTR(CMODEL, SCALE, SSQRW)  
RETURN  
END  

C SUBROUTINE LAPTR(CMODEL, SCALE, SSQRW)  
INTEGER IN, ND2, N1, N2, NPAR, IFORCE, NSQRWV, ICALL  
REAL FSQR(513), SCALE, R, IM, SSQRW  
REAL FU, FL, VU, VL, AREA, L, POR, LVUD, D1, PAR1, PAR2, TPULSE, SF  
COMPLEX*8 CMODEL(1024), CDEN(513), ZN3, EP, EM, CCOSH, CSINH  
COMPLEX*8 S(513), S12(513), YEMF(1024), M1(513), FS(1024)  
COMPLEX*8 CC1(513), CC2(513), CC3(513)  
COMMON/INTERS/N, ND2, N1, N2, NPAR, IFORCE, NSQRWV, ICALL  
COMMON/REELS/S, S12, YEMF, M1, FS, CC1, CC2, CC3  
ICALL = ICALL + 1  
IF (ICALL.GT.1.AND.NPAR.NE.3) GO TO 20  
CALL FFUNCT(TPULSE)  
C SET VALUES FOR S = 0  
20 CDEN(1) = FL*LAPAR1*A2/AREA + FL/FU + 1.E0 + FL*LVUD/(D1*A2)  
CMODEL(1) = FS(1)/CDEN(1)  
C USE THE VALUE OF CMODEL(1) TO SCALE THE RESULTS IF SF = 0.E0  
IF (SF.GT.0.E0) GO TO 40  
SCALE = REAL(YEMF(1))/REAL(CMODEL(1))  
GO TO 80  
40 SCALE = SF  
80 CMODEL(1) = SCALE*CMODEL(1)  
R = REAL(YEMF(1))-REAL(CMODEL(1))  
I = AIMAG(YEMF(1))-AIMAG(CMODEL(1))  
FSQR(1) = R**2 + I**2  
DO 100 I = 2, N1  
ZN3 = PAR1*A1(I)  
EP = CEXP(ZN3)  
EM = CEXP(-ZN3)  
CCOSH = (EP+EM)/2.E0  
CSINH = (EP-EM)/2.E0  
CDEN(1) = (CC1(1)*PAR1+CC2(1)/PAR1)*CSINH+CC3(1)*CCOSH
CMODEL(I) = SCALE * CEXP(-S(I) * PAR2) * FS(I) / CDEN(I)
R = REAL(YEMF(I)) - REAL(CMODEL(I))
I = AIMAG(YEMF(I)) - AIMAG(CMODEL(I))
FSQR(I) = R^2 + I^2

100 CONTINUE
SSQRW = 0.E0
DO 120 I = 2, ND2
120 SSQRW = SSQRW + FSQR(I)
120 CONTINUE
SSQRW = 2.E0 * SSQRW + FSQR(N1)
RETURN
END

C
SUBROUTINE FFUNCT(TPULSE)
INTEGER I, J, DIRECT
INTEGER N, ND2, N1, N2, IFORCE, NSQRWV, ICALL
REAL TPULSE, T1, TINJ, DT, XERT(1024), XEMT(1024), TAU
COMMON/S5(513), S12(513), YEMF(1024), M1(513), FS(1024)
COMMON/C1(513), C2(513), C3(513)
COMMON/INTERST, N, ND2, N1, N2, NPAR, IFORCE, NSQRWV, ICALL
COMMON/PER, XERT, XEMT, DT, TINJ, TAU
COMMON/IMGS, S, S12, YEMF, M1, FS, C1, C2, C3

C INITIALIZE FORCING FUNCTION FS
20 IF (IForce) 40, 180, 260
C IF IFORCE=0, A DISCRETE SQUARE WAVE PULSE IS USED
C IF NSQRWV = 0, THEN NSQRWV IS DETERMINED BY THE VALUE OF TINJ
40 IF (NSQRWV .NE. 0) GO TO 100
   NSQRWV = 1
   T1 = (NSQRWV - 1) * DT
   IF (T1 .GT. TINJ) GO TO 80
   NSQRWV = NSQRWV + 1
   GO TO 60
80 IF (TINJ .LT. (T1 - DT * 0.5)) NSQRWV = NSQRWV - 1
   IF (NSQRWV .EQ. 1) NSQRWV = 2
100 J = NSQRWV - 1
   DO 120 I = 1, NSQRW
      XEMT(I) = 1.E0 / (NSQRWV * DT)
      IF (NSQRWV .GT. 2) XEMT(I) = 1.E0 / (J * DT)
120 FS(I) = CMPLX(XEMT(I), 0.E0)
   IF (NSQRWV .LE. 2) GO TO 140
   XEMT(I) = XEMT(I) / 2.E0
   XEMT(NSQRWV) = XEMT(I)
   FS(I) = CMPLX(XEMT(I), 0.E0)
   FS(NSQRWV) = CMPLX(XEMT(NSQRWV), 0.E0)
140 J = NSQRWV + 1
   DO 160 I = J, N
      XEMT(I) = 0.E0
160 FS(I) = CMPLX(XEMT(I), 0.E0)
   TPULSE = (NSQRWV - 1) * DT
   GO TO 300
C IF IFORCE=1, AN ANALYTICAL SQUARE WAVE PULSE IS USED
C IF TPULSE=0, THE VALUE OF TINJ IS USED FOR TPULSE
180 IF (TPULSE.NE.0.E0) GO TO 200
   TPULSE=TINJ
200 FS(1)=CMPLX(1.E0,0.E0)
   DO 220 I=2,N1
220 FS(I)=(1.E0-CEXP(-S(I)*TPULSE))/(S(I)*TPULSE)
   IF (ICALL.GT.1) GO TO 499
   DO 240 I=1,N
240 XEMT(I)=0.E0
   GO TO 499
C IF IFORCE=2, BYPASS DATA IS USED
260 DO 280 I=1,N
280 FS(I)=CMPLX(XEMT(I),0.E0)
300 DIRECT=1
   CALL FFT(FS,N,DIRECT,DT)
C TAUTCQ IS THE FIRST-ORDER TIME CONSTANT FOR THE TCD
   IF (TAUTCQ.LE.0.E0) GOTO 340
499 DO 320 I=1,N1
320 FS(I)=FS(I)/(1.E0+S(I)*TAUTCQ)
340 RETURN
END

ENTRY
   2 0 1 01.000000
   -0 -0
   512 256 00.133333
   0 0 0
   0200 3 3
   0 0 1
   1067.0000 +50
   1018.0000 +50
   00.005000
   02.000000
   00.700000
   1.0000
   00.701000
   1.0000
   0.0000
   16 1000 4
   1
0000
0.1000000E-02 0.1000000E+01 1.0000000E+01

EXPLANATION OF VARIABLES AND SUBROUTINES USED IN MINIMIZATION
PROGRAM ZXMIN(W)7

VERSION 6 IS SIMILAR TO VERSION 5 ONLY IT ALLOWS THE OPTION OF
TREATING THE REGION BETWEEN THE TOP OF THE PELLET AND THE TRACER DISPERSION CONE AS A REGION OF IDEAL MIXING (FRACTM = 1) OR AS A REGION OF PURE GASEOUS DIFFUSION (FRACTM = 0)

SIGNIFICANT, BUT OBVIOUS, CHANGES IN THE NOMENCLATURE HAVE BEEN IMPLEMENTED IN THIS VERSION OF THE PROGRAM

VERSION 7 ALLOWS THE INCLUSION OF THE FIRST-ORDER TCD TRANSFER FUNCTION TO BE INCLUDED IN THE MODEL. TAUTCD IS THE TIME CONSTANT FOR THE TRANSFER FUNCTION

C NDATA-THE NUMBER OF DATA POINTS INITIALLY
C NTOTAL-THE FIRST NTOTAL OF NDATA VALUES ARE USED
C NMAX-THE NUMBER OF DATA POINTS USED
C NRUN-DYNAMIC RUN NUMBER
C NBYPAS-BYPASS DATA RUN NUMBER
C NPLT-PELLET NUMBER
C NSQRWV-THE NUMBER OF POINTS USED IN A DISCRETE SQUARE WAVE PULSE
C TPNPULSE-THE INJECTION TIME IN AN ANALYTICAL SQUARE WAVE PULSE
C DTTDATA-THE TIME SPACING BETWEEN THE RAW DATA
C DT-THE TIME SPACING BETWEEN THE MODIFIED DATA POINTS
C FU,FL-THE UPPER AND LOWER GAS FLOW RATES
C FLS,FLTCD-FOR SPLIT FLOW, THE SPLIT AND TCD FLOW RATES
C VU,VL-UPPER AND LOWER CHAMBER VOLUMES
C VDU,VL-UPPER AND LOWER TUBING DEAD VOLUMES
C VDLTCD-FOR SPLIT FLOW, EQUALS THE DEAD VOLUME TO THE TCD
C VCONE-CONE VOLUME
C VLOOP-SAMPLE LOOP VOLUME
C VGCV-INTERNAL VOLUME OF GC VALVE
C VINU-INJECTION VOLUME = VGCV + VLOOP
C VSBFU-VOLUME OF SOAP BUBBLE FLOW METER USED TO MEASURE FU FLOW
C VSBFL-VOLUME OF SOAP BUBBLE FLOW METER USED TO MEASURE FL FLOW
C VSBFLS-VOLUME OF SOAP BUBBLE FLOW METER USED TO MEASURE FLS FLOW
C TFU-TIME FOR SOAP BUBBLE TO TRAVEL THROUGH VOLUME VSBFU
C TFL-TIME FOR SOAP BUBBLE TO TRAVEL THROUGH VOLUME VSBFL
C TFLS-TIME FOR SOAP BUBBLE TO TRAVEL THROUGH VOLUME VSBFLS
C LRING-LENGTH OF PELLET HOLDING RING
C L-PELLET LENGTH
C LCONE-DEPTH OF CONE INTO RING
C LVU-HEIGHT OF CONE ABOVE PELLET, = LRING-L-LCONE
C FRACTM-FRACTION OF LVU VOLUME IDEALLY MIXED
C LVUM-FRACTIONAL LENGTH OF LVU FOR IDEAL MIXING = FRACTM*LVU
C LVUD-FRACTIONAL LENGTH OF LVU FOR PURE DIFFUSION = LVU-LVUM
C D-EFFECTIVE DIFFUSIVITY
C D1-DIFFUSION COEFFICIENT OF GASES THROUGH LVUD
C POR-PELLET POROSITY
C POR1-POROSITY OF LVU REGION, = 1 FOR GASES
C TLAGD-LAG-TIME FOR THE DYNAMIC DATA
C TLAGM-LAG-TIME FOR MOMENTS=TLAGD+TINJ/2
C YERT-THE RAW EXPERIMENTAL DATA, TIME DOMAIN
C YEMT-THE MODIFIED EXPERIMENTAL DATA, TIME DOMAIN
C YEMF-THE FT OF THE MODIFIED EXPERIMENTAL DATA
C YM0DEL-THE NEW ESTIMATE OF THE DATA USING THIS PROGRAM'S PROCEDURE
C PAR(I)-THE ITERATION PARAMETERS
C NEWPAR(3)-THE NEW VALUE OF THE ITERATION PARAMETERS
C S-THE LAPLACE TRANSFORM VARIABLE
C S12-SQRT(S)
C KMAX-MAXIMUM NUMBER OF FUNCTION EVALUATIONS ALLOWED
C XERT-FORCING FUNCTION, TIME DOMAIN
C XEMT-MODIFIED FORCING FUNCTION, TIME DOMAIN
C FS-COMPLEX FORCING FUNCTION
C ATNB,ATND-TCD ATTENUATIONS FOR BYPASS AND DYNAMIC DATA
C AMPB,AMPD-SA-1 AMPLIFICATIONS FOR BYPASS AND DYNAMIC DATA
C RESB,RESD-RESOLUTION FOR BYPASS AND DYNAMIC DATA (4=HIGH RES)
C FORCE=0 A DISCRETE SQUARE WAVE PULSE IS USED
C =1 AN ANALYTICAL SQUARE PULSE IS USED.
C =2 BYPASS DATA USED
C SF-SCALE FACTOR
C SPLIT-IF SPLIT .NE. 0, THE FLOW IS SPLIT BEFORE GOING TO THE TCD
C DATA HANDLING OPTIONS
NDATA-NUMBER OF INPUT DATA POINTS. MUST BE GREATER THAN NTOTAL. BYPASS
DATA MUST HAVE SAME NUMBER OF DATA POINTS.
DTDATA-TIME SPACING BETWEEN INPUT DATA POINTS. BYPASS DATA MUST HAVE
SAME TIME SPACING.
NTOTAL-THE FIRST 'NTOTAL' DATA POINTS OF THE INPUT DATA FILE WILL BE
READ. MUST BE LESS THAN OR EQUAL TO NDATA AND EQUAL TO 64,
128, 256, 512, OR 1024.
NMAX-MAXIMUM NUMBER OF DATA POINTS TO BE USED FROM THE 'NTOTAL'
POINTS USED. WHEN REDUCING THE DATA SET FROM NTOTAL POINTS
TO NMAX POINTS, DATA POINTS ARE PICKED AT AN APPROPRIATE TIME INTERVAL SO THE DATA COVERS THE SAME
TOTAL TIME SPAN. USING NMAX LESS THAN NTOTAL IS EQUIVALENT
TO HAVING A SLOWER SAMPLING RATE. MUST BE EQUAL TO 64, 128,
256, 512, OR 1024.
FOR NMAX < 0, THE DATA SET IS TRUNCATED TO NMAX DATA POINTS.
THIS IS USED FOR THE RAW EXPERIMENTAL AND RAW BYPASS DATA SO THE PROPER VALUES ARE PRINTED AS OUTPUT IF THE MODIFIED DATA
SET IS TRUNCATED TO LESS THAN NTOTAL POINTS.
NSMTH- THE NUMBER OF TIMES THE EXPERIMENTAL DATA WILL BE SMOOTHED
USING A 9-POINT SMOOTHING ROUTINE. IF NSMTH < 0, THE DATA
WILL BE SMOOTHED UNTIL A CONSTANT TRUNCATION TIME, AS
DETERMINED BY PMAX, IS OBTAINED. THIS IS VALID ONLY FOR
PMAX BETWEEN 500 AND 1000, AND 1500 AND 2000. THE MAXIMUM
NUMBER OF SMOOTHINGS PERFORMED WHEN TRYING TO DETERMINE A
CONSTANT TRUNCATION TIME IS 100+NSMTH. IF THE DATA IS
SMOOTHED ABS(NSMTH) TIMES, THE VALUE RETURNED FROM THE
SUBROUTINE WILL BE -100+NSMTH. SEE PMAX FOR MORE INFORMATION.
NSMTHB-SIMILAR TO NSMTH ONLY THIS PARAMETER APPLIES TO THE BYPASS DATA.
PMAX- THIS PARAMETER CONTROLS THE TRUNCATION POINT FOR THE
EXPERIMENTAL DATA. FOR PMAX BETWEEN 0 AND 500, THE PROGRAM WILL ZERO ALL DATA AFTER 'PMAX' SECONDS. FOR PMAX BETWEEN 500 AND 1000, THE PROGRAM WILL ZERO ALL THE DATA TRAILING THE FIRST DATA POINT WHOSE AVERAGE VALUE IS LESS THAN YM\textsuperscript{X} (PMAX - 500) / 100, WHERE YM\textsuperscript{AX} IS THE MAXIMUM VALUE IN THE DATA SET. BY ADDING 1000 TO THE VALUE OF PMAX, ALL DATA VALUES WILL BE SHIFTED DOWN BY THE AVERAGE VALUE OF THE LAST NON-ZERO DATA VALUE. THIS PREVENTS A DROP-OFF IN THE TAIL OF THE DATA AND A TAIL WHICH MAKES A SMOOTH TRANSITION TO A ZERO BASELINE.

NBASE - THIS VALUE AVERAGES 'NBASE' DATA POINTS AND USES THIS AVERAGE TO SHIFT ALL THE DATA TO ROUGHLY GET A ZERO BASELINE. FOR NBASE > 0, THE LAST NBASE DATA VALUES ARE AVERAGED. IF NBASE < 0, THE FIRST NBASE VALUES ARE AVERAGED TO DETERMINE THE BASELINE. FOR NBASE > 1000, THE FIRST (NBASE - 1000) DATA POINTS AFTER ITAIL ARE AVERAGED.

PMAXB - SIMILAR TO PMAX EXCEPT THIS PARAMETER IS USED FOR BYPASS DATA.

NBASEB - SIMILAR TO NBASE EXCEPT THIS PARAMETER IS USED FOR BYPASS DATA.

OTHER PARAMETERS.

ESTMT - THIS CONTROLS THE INITIAL ESTIMATE OF THE LAG-TIME, TLAG. IF = 0, TLAG IS DETERMINED FROM THE DEAD VOLUMES AND FLOW RATES AS DONE IN THE METHOD OF MOMENTS. IF ESTMT = 1, LTAE READ IN AS INPUT IS USED FOR THE INITIAL ESTIMATE FOR ITERATIONS. ON OUTPUT, THE VALUE MAY BE EQUAL TO 2. THIS INDICATES THAT THE OPTION OF USING THE VALUE OF TLAG FROM IMPULSE RESULTS HAS OCCURRED.

ESTMD - THIS CONTROLS THE INITIAL ESTIMATE OF D USED FOR THE ITERATIONS. IF EQUAL TO 0, D IS DETERMINED AS IN THE METHOD OF MOMENTS. IF ESTMD = 1, D READ IN AS INPUT IS USED FOR THE INITIAL ESTIMATE FOR ITERATIONS. ON OUTPUT, THE VALUE MAY BE EQUAL TO 2. THIS INDICATES THAT THE OPTION OF USING THE VALUE OF D FROM IMPULSE RESULTS HAS OCCURED.

AMPBM - THE M STANDS FOR MULTIPLIER AND AMPBM IS MULTIPLIED BY THE VALUE OF AMPB. IF THE SCALE FACTOR DETERMINED BY THE ATTENUATIONS AND AMPLIFICATIONS OF THE DYNAMIC AND BYPASS RUNS IS DESIRED, SET AMPBM TO 1. IF THE SCALING PROCEDURE OF EQUATING ZERO TH MOMENTS IS DESIRED, SET AMPBM TO 0.

OUTPUT OPTIONS

OUTMOD - THIS DETERMINES IF THE MODIFIED EXPERIMENTAL DATA IS TO BE PRINTED TO A DATA FILE. IF OUTMOD EQUAL 0, THE DATA ARE NOT PRINTED. IF OUTMOD EQUAL 1, THE DATA ARE PRINTED TO A FILE.

OUTFIT - THIS DETERMINES IF THE MODEL'S FIT TO THE EXPERIMENTAL DATA IS TO BE PRINTED TO A DATA FILE. IF OUTFIT EQUAL 0, THE DATA ARE NOT PRINTED. IF OUTFIT EQUAL 1, THE DATA ARE PRINTED TO A FILE.

PARTS OF THE MODEL'S RESULTS ARE PRINTED DURING OUTPUT. IF OUTPRT EQUAL 1, THE VALUES ARE PRINTED. IF OUTPRT EQUAL 0, THE PRINTING OF DATA IS OMITTED.

ZXMIN OPTIONS

KMAX - THIS IS THE MAXIMUM NUMBER OF FUNCTION EVALUATIONS, CALLS TO THE SUBROUTINE, ALLOWED.

I0PT - THIS OPTION DETERMINES HOW THE HESSIAN MATRIX IS ESTIMATED. FOR I0PT=0, THE HESSIAN MATRIX IS INITIALIZED TO THE IDENTITY MATRIX. FOR I0PT=2, THE ROUTINE WILL ESTIMATE THE DIAGONAL ELEMENTS OF THE HESSIAN MATRIX. FOR I0PT=3, AN ESTIMATE OF THE HESSIAN MATRIX IS MADE. ALTHOUGH THE ZXMIN ROUTINE CAN USE A USER SUPPLIED ESTIMATE OF THE HESSIAN MATRIX, I0PT=1, THIS IS NOT AN OPTION IN THIS PROGRAM.

NSIG - THIS IS THE CONVERGENCE CRITERIA PARAMETER. THIS IS THE NUMBER OF DIGITS OF ACCURACY REQUIRED IN THE PARAMETER ESTIMATES. ITERATIONS ARE STOPPED IF THE PARAMETERS AGREE TO NSIG DIGITS. LEADING ZEROS TO THE RIGHT OF THE DECIMAL POINT ARE COUNTED WHEN COMPUTING NSIG.

FORCING FUNCTION OPTIONS

IFORCE - THIS PARAMETER DETERMINES THE SHAPE OF THE FORCING FUNCTION TO BE USED. FOR IFORCE=0, A DISCRETE SQUARE WAVE USING NSQRWV DISCRETE TIME DATA VALUES ARE USED. THE AREA OF THE SQUARE WAVE IS NORMALIZED TO 1.0. FOR NSQRWV=1, THIS GIVES THE RESULTS EQUIVALENT TO AN IMPULSE FUNCTION. AFTER INITIALIZING THE SQUARE WAVE, THE TRANSFORM TO THE FREQUENCY DOMAIN IS PERFORMED USING THE FFT PROCEDURE. IF IFORCE=1, A CONTINUOUS SQUARE WAVE FUNCTION IS USED. THE LAPLACE TRANSFORM FOR A SQUARE WAVE IS USED AND NO TRANSFORMATION PROCEDURE IS NEEDED. AN ADVANTAGE OF USING THIS FORM FOR THE SQUARE WAVE IS THAT THE PULSE TIME OF THE SQUARE WAVE NEED NOT BE AN INTEGER MULTIPLE OF THE TIME SPACING PARAMETER DT. FOR IFORCE=2, DATA FROM A BYPASS RUN IS USED AS THE FORCING FUNCTION. IT IS UP TO THE USER TO DETERMINE THE APPROPRIATE BYPASS FUNCTION TO BE USED FOR THE RUN.

NPAR - THIS IS THE NUMBER OF PARAMETERS TO BE USED FOR THE ITERATIONS. INITIAL ESTIMATES FOR D AND TLAGD ARE DETERMINED BY THE VALUES OF ESTAD AND ESTMT. THE FORCING FUNCTION USED IS DETERMINED BY THE VALUE OF IFORCE. FOR NPAR=0, THE PROGRAM WILL PERFORM NO ITERATIONS AND WILL EVALUATE ALL THE RESULTS WITH THE VALUES OF D, TLAG, ETC. DETERMINED BY THE OTHER PROGRAM VARIABLES. FOR NPAR=1, THE PROGRAM WILL ITERATE ON 1/SQRT(D), PAR(1). FOR NPAR=2, THE PROGRAM WILL ITERATE ON PAR(1), AND TLAGD, PAR(2).
FOR NPAR=3, THE PROGRAM WILL ALSO ITERATE ON TPULSE, PAR(3) - THE CONTINUOUS SQUARE WAVE PULSE TIME. THE VALUE OF TPULSE INPUT TO THE PROGRAM IS USED AS THE INITIAL ESTIMATE FOR TPULSE IF TPULSE .NE. 0. IF TPULSE = 0, THE VALUE OF TINJ IS USED AS THE INITIAL ESTIMATE OF TPULSE. THE INITIAL VALUES OF D AND TLAG ARE STILL DETERMINED BY ESTMD AND ESTMT, BUT IFFORCE MUST BE 1.